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JOURNAL OF RESEARCH
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RESEARCH PAPER RP699

Part of Journal of Research of the National Bureau of Standards, volume 13
August 1934

DERIVATION OF PHOTOMETRIC STANDARDS FOR TUNGSTEN-FILAMENT LAMPS

By H. T. Wensel, Wm. F. Roeser, L. E. Barbrow, and F. R. Caldwell

ABSTRACT

A method is described for comparing the candlepower of carbon lamps with that of tungsten lamps which avoids the usual difficulties of heterochromatic photometry. The method is based on photometric comparisons of carbon lamps with a black body immersed in freezing platinum and of gas-filled tungsten lamps with a black body immersed in freezing iridium. The relative integral brightness of the two black bodies is calculated from the ratio of brightness measured at one wave length with an optical pyrometer.

The method was used to calibrate six tungsten-filament gas-filled standard lamps, operating at a color temperature of 2,727 K, on the basis of the carbon primary standards, which operate at a color temperature of 2,097 K. The step-up as made is applicable to the International Commission on Illumination standard observer with an accuracy certainly better than 1 percent. A comparison with the vacuum tungsten standards maintained at the National Bureau of Standards since 1911, yielded results agreeing within 1 percent.

An empirical formula is given for the brightness of a black body over the range 1,550 to 2,727 K.

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I. INTRODUCTION

The unit of luminous intensity is defined in terms of the average light emission, in a specified horizontal direction, of a number of carbon-filament incandescent lamps each operating at a specified voltage. Groups of such standards of horizontal candlepower are in the custody of the several national standardizing laboratories and periodic intercomparisons have indicated that there are no discrepancies of more than a few tenths of a percent among these various groups. If, therefore, these standards are changing with time, the various groups are changing at substantially the same rate. It is believed that the drift in the unit, up to the present time, has been small.

Practically all lamps now in commercial use are tungsten lamps of either the vacuum or gas-filled type. The spectral-energy distribu-

tion of the light from these lamps differs from that of the light from the carbon-filament standards chiefly because of the higher filament temperatures. For rating tungsten lamps, the various national standardizing laboratories maintain tungsten-filament auxiliary standards, which have been "stepped-up" from the carbon standards. This step-up has been made independently in each country and the resulting tungsten standards of the various national laboratories are not in good agreement. This condition is traceable to the difficulties of heterochromatic photometry involved.

The unit of light is of such a nature that, when defined for light of a given quality or spectral distribution, an additional specification of the characteristics of the observer's eye is required before the unit can be used to evaluate light of any other quality. This specification is accomplished by selecting a set of factors which express the relative visibility of radiation of the various wave lengths for a selected (hypothetical) observer.

The visibility of radiant energy was measured by Gibson and Tyndall [1] for 52 observers; their recommended average values, taking into account previous work as well as their own have been used by the International Commission on Illumination to define a standard [2] observer. All actual observers depart more or less from this definition. As an illustration consider the two observers designated by Gibson and Tyndall as 15 and 19, respectively, who represent extreme departures although both have normal color vision. If one-half of a photometric field is illuminated with light of wave length 0.50μ and the other half with light of wave length 0.65μ in such amounts that the ICI standard observer would judge the two halves of the field to be equally bright, observer 15 would judge the green half to be over twice as bright as the red, and observer 19 would judge the red half to be more than 2½ times as bright as the green.

The carbon standards emit light of approximately the same quality as a hollow inclosure, or so-called "black body", at a temperature [3] of 2,100 K. Suppose we have a tungsten-filament lamp which to the ICI standard observer appears to have the same intensity as one of the carbon lamps which define the unit. The ICI observer evaluates the excess light from the carbon lamp in the red end of the spectrum as equal to the excess from the tungsten lamp in the blue end of the spectrum. It is quite obvious, however, that the tungsten lamp has a greater intensity for the observer designated by Gibson and Tyndall as no. 15, while the reverse is true for observer no. 19.

It is meaningless, therefore, to derive photometric standards for tungsten lamps from the carbon standards without specifying the observer to whom the derivation applies. Such derivations have always been made in terms of some "average observer", but confusion has sometimes resulted from a failure to indicate clearly the visibility factors actually used. The use of the same factors by everyone is of more importance than the factors themselves (within reasonable limits). Since the adoption by the International Commission on Illumination of the values recommended by Gibson and Tyndall, there no longer exists any reason for such confusion and the use of the ICI standard observer is now practically universal.

[1] K. S. Gibson and E. P. T. Tyndall. B.S. Sci.Pap. 19,131(1923-24); S475.
[2] Recueil des Travaux, I.C.I. 16th session (Geneva), 67(1924).
[3] Those in the custody of the National Bureau of Standards have an average color temperature of 2,097 K when operating at the specified voltages.

II. METHODS AVAILABLE

In the past, 3 general methods have been used to make the step-up from carbon standards to tungsten standards. The 2 types of lamps have been compared directly by means of a Lummer-Brodhun or similar photometer, making it necessary to tolerate a large color difference in the photometric field. Under such conditions accurate measurements are out of the question and the method yields, at best, an approximate check on other methods.

The second method is to compare the 2 types of lamps by means of a flicker photometer, the criterion of brightness equality being the disappearance of flicker in the field. Some question has at various times been raised as to the theory underlying the flicker method. This method gives satisfactory precision, however, and its use is justified because it gives results in agreement with those obtained with other methods. In both of these methods, the visual characteristics of the individuals making the comparisons must be known in order to reduce the results to the basis of the average observer.

In the third method the color difference is eliminated from the photometric field by placing a blue filter in front of the carbon lamp. If the spectral distribution of the light in the 2 halves of the field is nearly the same, the characteristics of the observer's eye have a negligible effect and need not be known. The light transmission, t, of each filter i.e., the ratio of the transmitted to the incident light may be calculated from the measured spectral transmission, t_λ, the approximate color temperature θ of the incident light, and any desired set of visibility factors, V_λ, by means of the formula

$$t = \frac{\int_0^\infty \lambda^{-5} e^{-\frac{C_2}{\lambda\theta}} V_\lambda t_\lambda d\lambda}{\int_0^\infty \lambda^{-5} e^{-\frac{C_2}{\lambda\theta}} V_\lambda d\lambda} \qquad (1)$$

The filter method has one decided advantage in that a particular filter may be circulated among several different laboratories to determine the differences obtained in stepping-up from one color temperature to another. If these laboratories then agree to use the same filter to set up tungsten standards and also agree to use the same value for the transmission, discrepancies in the resulting tungsten standards should not be appreciably greater than those in the carbon standards. Steps [4] have been taken to bring the tungsten standards of England, France, Germany, and the United States into agreement through the distribution of such filters. Four blue-glass filters have been circulated among the national laboratories of the countries named where their transmissions have been determined. On the basis of these determinations agreement has been reached on the transmissions to be assigned to each of the filters, one of which is retained by each of the 4 laboratories concerned. The transmissions of these 4 filters relative to each other have been very accurately determined and it is highly probable that the absolute values agreed upon apply closely to the ICI observer.

The present work was undertaken to furnish an independent check on the absolute values assigned to these filters and was completed

[4] Procès-Verbaux des Seances, Comité Int. d. Poids et Mes. 6, 324(1933).

before final agreement on these values had been reached. The results of the present work were transmitted in the form of a memorandum in July 1931 to the Advisory Committee on Electricity and Photometry of the International Committee of Weights and Measures and were later presented before the Optical Society of America at its Rochester meeting[5] on October 22, 1931. Copies of the memorandum of July 1931 were distributed to a considerable number of interested scientists. The method therein described was proposed 2 years later by Ribaud [6] who however reports no experimental work.

III. METHOD USED

Consider two black bodies, one matching in color the carbon standards and the other matching in color a tungsten lamp the candlepower of which is to be determined. The brightness of the first, B_1, may be measured by comparing it with the carbon standards as described elsewhere.[7] If now we measure the ratio of brightness of the 2 black bodies at some known wave length by means of an optical pyrometer, the brightness, B_2, of the second black body may be calculated if the temperature of one of the black bodies is known; a photometric comparison of the second black body with the tungsten lamp will then yield a value for the candlepower of the latter.

Let θ_1 and θ_2 = the respective temperatures in degrees K
B_1 and B_2 = the respective brightnesses
λ = wave length, in microns
R_o = ratio of brightness measured at wave length λ_o
V_λ = relative visibility (for ICI observer)
C_2 = second constant in Wien's law = 14,320 micron degrees.

Then

$$\frac{1}{\theta_2}=\frac{1}{\theta_1}-\frac{\lambda_o \log_e R_o}{14{,}320} \tag{2}$$

$$\frac{B_2}{B_1}=\frac{\int_o^\infty \lambda^{-5} e^{-\frac{14{,}320}{\lambda\theta_2}} V_\lambda d\lambda}{\int_o^\infty \lambda^{-5} e^{-\frac{14{,}320}{\lambda\theta_1}} V_\lambda d\lambda} \tag{3}$$

and

$$\frac{B_2}{B_1}=\frac{\int_o^\infty \lambda^{-5} e^{\left(\frac{\lambda_o}{\lambda}\log_e R_o-\frac{14{,}320}{\lambda\theta_1}\right)} V_\lambda d\lambda}{\int_o^\infty \lambda^{-5} e^{-\frac{14{,}320}{\lambda\theta_1}} V_\lambda d\lambda} \tag{4}$$

It is of course essential that the temperature of each black body during the photometric comparisons shall be the same as that during the optical-pyrometer determinations. This can best be assured by using black bodies immersed in freezing metals. If freezing metals are to be used, platinum is the most suitable for securing a color match with the carbon standards. The upper temperature permits of some choice. The rhodium point,[8] 2,239 K, is scarcely high enough to furnish a real test of the method. The iridium point, however, seems to be ideal. It is near the upper limit at which tungsten lamps may be

[5] J. Opt. Soc. Am. 22,7(1932).
[6] Comptes Rendus 196,687–688(1933).
[7] Wensel, Roeser, Barbrow, and Caldwell, BS J.Research 6,1103(1931); RP325.
[8] Roeser and Wensel, BS J.Research 12,518(1934); RP676.

operated without rapid deterioration. Moreover, iridium may be melted and frozen in air while rhodium must be used in vacuo. The filters which have been distributed to the national laboratories convert light of 2,100 K color temperature to light whose color temperature is about 2,400 K. To step up from the carbon standards to the iridium point, therefore, the filters must be used twice and in so doing the percentage error in the filter transmission produces twice this error in the final result. Once it has been determined that the filters can be used to make this double step without serious error, they may be depended upon for the intermediate point.

IV. FREEZING POINTS OF PLATINUM AND IRIDIUM

The freezing point of platinum [9] has been determined as 2,046.6 K (1,773.5 C) with an uncertainty not exceeding 1° K and that of iridium [10] as 2,727 K (2,453.8 C) with an uncertainty not exceeding 3° K. These determinations were each made upon the same black bodies used in the present photometric work and could be used to calculate B_2/B_1 from equation 3. These values of temperature were each obtained by measuring the ratio of brightness for red light relative to the gold point. Although uncertainties in these values do not exert their full effect in the present case because that portion of the uncertainty due to lack of purity of the metals and to temperature differences between the metal and the black body have no effect, a value of B_2/B_1 calculated by equation 3 would scarcely be accurate to 1 percent. However, in the determination of the freezing point of iridium, the ratio of brightness of the black body immersed in the freezing iridium relative to the one immersed in the freezing platinum was measured directly for wave length 0.652μ. This permits calculation by the use of equation 4 in which θ_1, the freezing temperature of the platinum need be known only approximately since a change of 100° K in θ_1 produces a change of only 1 percent in $\frac{B_2}{B_1}$. The value $\lambda_o \log_e R_o$ was determined as 1.7480 with an uncertainty not greater than 0.0008, neglecting the 2 factors mentioned which do not affect the present work. The ratio $\frac{B_2}{B_1}$, was therefore determined with an uncertainty of somewhat less than 0.5 percent.

V. PHOTOMETRIC MEASUREMENTS

The comparison between the primary carbon standards of the National Bureau of Standards and the black body immersed in freezing platinum has been described elsewhere.[11] The comparisons between the tungsten lamps and the black body immersed in freezing iridium were made in the same manner. The high melting point of iridium required special treatment of the crucible before use as described in the paper on the freezing point.

The tungsten lamps used were six 500-watt, 110-volt, monoplane-filament projection lamps in a special T–20 bulb, with medium screw skirted base. The over-all length was 9½ in. and the distance from the

[9] Roeser, Caldwell, and Wensel, BS J.Research 6, 1119(1931);RP326.
[10] Henning and Wensel, BS J.Research 10, 809(1933); RP568.
[11] Wensel, Roeser, Barbrow, and Caldwell, BS J.Research 6, 1103(1931);RP325.

center of the filament to the tip of the globe was 5½ in. The special T–20 bulb used is 4 in. longer than that of the regular lamp, the filament being in the same position relative to the base. Life tests made on a group of the regular lamps indicated a satisfactory degree of constancy at color temperature 2,800 K, some blackening occurring at the top of the bulb. The special lamps with T–20 bulbs were then resorted to in order to remove the part of the bulb suffering the blackening from the region of the filament.

These 6 lamps, operating at a color temperature of approximately 2,727 K, were compared, both before and after the black-body comparisions, with the vacuum tungsten standards [12] which have been maintained at the National Bureau of Standards since 1911. Their average candlepower was found to be 402.4 before and 398.4 after the black-body comparisions, a change which might be attributed to an actual change in the lamps. It is unlikely, however, that such a change occurred in these lamps in the very short time that they were used during this work. They were operated at only 75 volts while their rated voltage is 110 (at which their life is 50 hours). Life tests on similar lamps indicated that no appreciable changes occur even after several hundred hours of use at 75 volts. It is perhaps unfortunate that more observations were not taken on these lamps previous to their use in the comparisons with the black body, but this fact was realized only after the values obtained at the conclusion of the work were found to be 1 percent lower. However, the uncertainty in the final result of this comparison is only slightly greater than that of the final result of the black-body comparisons. The results of the photometric observations are given in tables 1 and 2.

TABLE 1.—*Candlepower of the 6 tungsten lamps by comparison with the NBS vacuum tungsten standards of 1911*

Comparison made	Observer			
	RPT	LEB	HTW	MEL
	c	c	c	c
Before	402.6	399.6	404.6	402.8
After	398.5	398.3	397.1	399.5
Mean	400.5	399.0	400.8	401.2

Average for all observers 400.4±3.0 candles.

TABLE 2.—*Candlepower of the 6 tungsten lamps derived from the primary carbon standards of the NBS*

[Step-up made with black bodies immersed in freezing platinum and iridium]

Observer		
HTW	WFR	FRC
c	c	c
397.2	397.0	396.2
397.4	394.6	398.3
394.2	396.7	397.3
393.1	393.6	398.3
395.5	395.5	397.5

Average for all observers 396.2±1.7 candles.

[12] At present, unfortunately, no data are available on the question of how these standards will agree with the standards which will result from the use of the filters for which transmission values have been agreed upon.

VI. DISCUSSION

The figures ±3.0 and ±1.7 c given in tables 1 and 2 are each 5 times the probable error. This product has sometimes been called the "huge error" because it is an error such that the chance of occurrence of an equal or greater error is only one in a thousand. It is fairly certain that the accidental errors of photometric matching do not exceed these. The figure ±1.7 c, however, must be combined with the uncertainty in determining the ratio $\frac{B_2}{B_1}$ for the 2 black bodies used.

The ratio $\frac{B_2}{B_1}$, calculated for the ICI standard observer, is subject to about the same uncertainty as the measured ratio of brightness for wave length 0.652μ. This ratio was measured with a precision optical pyrometer giving complete disappearance of the filament with no color difference to bother the observer. The sector disk used had an angular opening of 25° of arc which was measured on a circular dividing engine to about 30″ of arc. The uncertainty in this measurement is, therefore, negligible. The uncertainty in the effective wave length is almost negligible, corresponding to not over 0.1 percent, while the value of C_2 used, 14,320μ deg., is estimated as uncertain by about 20, corresponding to an uncertainty of about 0.25 percent. The uncertainty in R_o, again 5 times the probable error, corresponds to 1.8 c.

The black-body comparisons are thus subject to the following uncertainties:

	c
Photometric comparisons	±1.7
Determination of R_o	1.8
λ_e	0.4
C_2	1.0
Square root of sum of squares =	±2.8

It would appear that the values derived for the NBS tungsten standards of 1911 should be lowered slightly to make them apply for the ICI standard observer. The difference, however, is just about on the border line of the experimental errors of the present work. At the time these standards were derived, the ICI observer had not yet been defined. In discussing the status of these Standards, Crittenden and Meyer [13] say "The assigned values are based on series of measurements made with the standard Lummer-Brodhun photometer by the group of observers then employed at the Bureau in photometric work" and that "the group of regular Bureau photometric observers was found to average very close to the normal observer as determined in these [14] tests." It may be considered, therefore, to a certain extent fortuitous that the 1911 derivation applies so closely to the ICI observer. In view of the excellent work which has been done on the transmission of the recently distributed filters, there is every reason to expect that the standards derived with the use of these filters will agree even more closely with the results obtained in the derivation by means of the black bodies.

[13] Proc. Int. Cong. on Ill. 1138 (1928).
[14] An average eye for heterochromatic photometry and a comparison of a flicker and an equality-of brightness photometer. Crittenden and Richtmyer, Bul.B.S., v. 14, 87(1918–1919).

VII. BRIGHTNESS OF BLACK BODIES AT OTHER TEMPERATURES

In calculating the ratio of brightness of 2 black bodies at temperatures θ_1 and θ_2, the usual formula, equation 3, page 164, is used.

The brightness of a black body at the platinum point is, without doubt, the best value to use as a base. It has been determined in 3 laboratories under conditions most favorable to high accuracy, namely upon black bodies immersed in freezing platinum. These determinations are listed in table 3.

TABLE 3.—*Brightness of a black body immersed in freezing platinum*

Date	Authority	Institution	Value reported
			C/cm²
1931	Wensel, Roeser, Barbrow, and Caldwell [1]	National Bureau of Standards	58.84
1933	Ribaud [2]	Faculté des Sciences de Strasbourg	58.78
1933	Report [3]	National Physical Laboratory	59.10
Mean value			58.91

[1] B.S.J.Research 6,1103(1931); R.P.325.
[2] Procès-Verbaux, Comité Int. d. Poids et Mes. 16,261(1933); Rev. d'Optique, 12,289(1933).
[3] Procès-Verbaux, Comité Int. d. Poids et Mes. 16,256(1933). The National Physical Laboratory Report for the Year 1933, p. 91 (issued 1934), in addition to mentioning the value 59.10 c/cm² previously reported, also reports additional observations on 60 melts and freezes yielding a value of 58.9 c/cm². This latter value is stated to be subject to revision pending further work.

The value of 58.9 c/cm² for a black body at 2,046.6 K leads to a value of 0.001602 watt per lumen for the least mechanical equivalent of light and the brightness, B, of any black body at temperature θ may be written

$$B=\frac{1}{0.001602\pi}\int_0^\infty J_\theta V_\gamma d\lambda \tag{5}$$

The relation between B and θ may be expressed by the following empirical formula which is very convenient for calculation.

$$B=2{,}495\left(\frac{\theta}{2{,}955}\right)^{\frac{461.4}{\sqrt{\theta}}} \tag{6}$$

The agreement between this empirical formula and the exact integral form, as shown in table 4, is better than one part in a thousand over the entire range from the platinum to the iridium point.

TABLE 4.—*Brightness of a black body as a function of temperature* (C_2=*14,320μ deg.*)

Temperature (degrees K)	Brightness		Temperature (degrees K)	Brightness	
	Equation 5	Equation 6		Equation 5	Equation 6
	C/cm²	*C/cm²*		*C/cm²*	*C/cm²*
1,550	1.273	1.297	2,200	137.0	137.0
1,600	2.077	2.107	2,239 [3]	167.1	167.1
1,650	3.295	3.330	2,250	176.1	176.1
1,700	5.091	5.130	2,300	223.9	223.9
1,750	7.679	7.720	2,350	282.0	282.0
1,800	11.33	11.37	2,400	351.7	351.7
1,828 [1]	14.02	14.06	2,450	434.9	434.9
1,850	16.38	16.42	2,500	533.3	533.3
1,900	23.24	23.27	2,550	648.8	648.8
1,950	32.41	32.42	2,600	783.7	783.6
2,000	44.46	44.47	2,650	940.1	939.8
2,046.6 [2]	58.91	58.91	2,700	1,121	1,120
2,050	60.09	60.09	2,727 [4]	1,227	1,227
2,100	80.09	80.08	2,728	1,231	1,231
2,150	105.4	105.4			

[1] Palladium point. [2] Platinum point. [3] Rhodium point. [4] Iridium point.

WASHINGTON, May 15, 1934

U.S. Department of Commerce National Bureau of Standards

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DEPENDENCE OF SOUND ABSORPTION UPON THE AREA AND DISTRIBUTION OF THE ABSORBENT MATERIAL

By V. L. Chrisler

ABSTRACT

This paper contains a report of work on sound absorption where large areas of absorbent material are installed. The measurements show that under these conditions it is impossible to obtain a logarithmic decay, hence the sound absorption is less than would be expected from the absorption coefficient of the material.

Measurements were also made on very small areas. In this case the absorption was more than would be expected from the coefficient determined by measuring the absorption of an area of 72 square feet.

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I. INTRODUCTION

The problem of measuring the sound absorption characteristics of materials and then making use of these measurements to compute the amount of material to be used in treating a room acoustically so as to obtain definite results is more complicated than was originally anticipated. When this problem was attacked by Wallace Sabine some 40 years ago, most of the rooms which he examined were fairly reverberant and the sound absorbing materials had low coefficients; but during the past few years there have been developed materials with much higher coefficients of absorption and there is a growing demand for acoustically dead rooms. As a result, it has been found

that some of the simplifying assumptions which were made and were approximately true for the older conditions are not sufficiently accurate for the treatments of modern problems in architectural acoustics, and doubts have arisen concerning the validity of both the laboratory methods of determining absorption coefficients and the manner in which the test results should be used in the acoustical treatment of auditoriums. The results of some experiments, which have recently been carried out at the National Bureau of Standards and are described in the present paper, throw some light on these difficulties.

The acoustic qualities of a room in a large measure depend upon the rate at which sound energy in it decays. After a room is completed this rate of decay can be measured, but the problem which must be solved, is, how to design a room so one is sure what its acoustic qualities will be after it is built.

The rate of decay of sound energy has been measured in many different kinds of rooms which were used for many different purposes. In general if the room is properly designed and the absorbent material properly placed so as to prevent echoes, flutters, etc., and if it has a given rate of decay, it can be predicted whether or not it will be acoustically satisfactory for a given use, as for example, an auditorium or a business office.

To know in advance of construction that a room will be acoustically satisfactory requires, therefore, that we know how to compute this rate of decay from the geometrical dimensions of the room and the acoustical properties of the materials used in its walls, ceiling, and floor, and in addition the acoustical properties of the furniture and other contents of the room. In attempting to solve this problem it is customary to make acoustical measurements of various materials, furniture, etc., in a reverberation chamber, and then, using a formula to compute certain numerical coefficients for the materials, furniture, etc., which will aid us in making the necessary prediction.

The formula[1] most commonly used, for surfacing materials, is the "Sabine formula" $T=\frac{.05V}{a_1s_1+a_2s_2+\ldots}$ where T is the reverberation time (in seconds); i.e., the time required for the sound to decay to $\frac{1}{1{,}000{,}000}$ of its original value, V the volume (in cubic feet) of the room (or sound chamber), s_1, s_2 ... the areas of the different surfaces (in square feet), and a_1, a_2 ... are called the sound absorption coefficients of these surfaces and $a_1s_1+a_2s_2$ ... is called the total absorption of the room (or chamber). Although in practice the process is simplified by a "calibration" of the chamber, in theory, the determination of the "absorption coefficient" of a surfacing material would consist in measuring the rate of decay of sound in the reverberation chamber with and without the presence of a known area of the material. From the two reverberation times so measured and the known dimensions of the chamber, the absorption coefficient would then be determined by substituting in the formula.

[1] This formula has been most generally used for computation purposes in the past. Other formulas have been derived by C. E. Eyring (Reverberation Time in Dead Rooms. The Journal of the Acoustical Society of America, vol. I, Jan. 1930), G. Millington (The Journal of the Acoustical Society of America, vol. IV, July 1932), and W. J. Sette (The Journal of the Acoustical Society of America, vol. IV, Jan. 1933). The ollowi ng discussion applies to all of these formulas.

To determine what effect a combination of materials would have in a room, the absorption coefficients so determined are substituted in the same formula using the volume of the room and the respective areas as given by the design. The reverberation time computed in this way is expected to give some idea of the reverberation time which the room would have after it is constructed.

In deriving this formula certain assumptions are made as follows:

(1) The reflected sound energy flux over any portion of the surface is a definite fraction $(1-a)$ of the incident sound energy flux, where a is defined as the absorption coefficient of the material.

(2) The sound absorption coefficient of a material is independent of the intensity of the sound.

(3) The sound energy flux incident upon the boundary surfaces of the air space enclosed in the room or chamber is uniform over all the boundary surfaces, or in other words there is a diffuse distribution of sound energy.

From these assumptions it follows:

(a) The decay of sound energy in an enclosure will be logarithmic.

(b) The absorption of a given material will be proportional to its area.

Up to the present time for the materials used, there is no experimental evidence to indicate that the second assumption is not correct. When the absorption of a material is small the other two assumptions are approximately correct, but as the absorption becomes larger the third assumption ceases to be even a rough approximation in most cases. The condition assumed under (3) can be partly controlled by the experimenter, but it has been found that even in a reverberation chamber, where the source is rotating and rotating vanes are installed, it is impossible, when the sample is highly absorbent, to meet exactly this third condition.

As a result of this inability to meet condition (3), when measurements are made in a reverberation chamber, the coefficient which is computed, in general, cannot represent the coefficient as defined by assumption (1) upon which the formula was based; that is, the fractional part of the incident energy which is absorbed at a single reflection. Furthermore, absorption coefficients of highly absorbent materials determined by any method which locates only two points on the decay curve, are inadequate for purposes of design.

II. EFFECT OF A LARGE AMOUNT OF ABSORPTION ON ONE SURFACE

1. EXPERIMENTAL RESULTS

We will now proceed to discuss the results of certain recent experiments [2] which have been carried out in the reverberation chamber at the National Bureau of Standards. As the dimensions of this room probably affect the results to some extent, it is desirable to restate them. The floor is approximately 25 ft. by 30 ft. and the ceiling height is 20 ft. In these reverberation chamber measurements, every possible attempt has been made to fulfill the condition (3) assumed in the derivation of the formula. Curve 1 in figure 1 shows that in

[2] A description of the equipment used will be found in BS Research Paper RP459, "An Automatic Reverberation Meter for the Measurement of Sound Absorption."

the empty room a logarithmic decay is obtained within experimental error. It was also found that, when a sample of 72 sq ft having a small coefficient of absorption was placed in the chamber, the decay of sound energy in the chamber was still logarithmic within experimental error but, when a highly absorbent sample of 72 sq ft was used the decay was no longer logarithmic as shown in curve 2 of figure 1.

As this decay was not logarithmic it was assumed there was not a diffuse distribution of sound energy, hence it was decided to install rotating vanes.[3] Figure 2 shows the interior of the reverberation chamber and gives some idea of the relative size of the vanes and chamber. The loud speakers are mounted in the vanes which serve as baffles. Also, the speakers rotate with the vanes and these moving sources tend to give a more uniform distribution of the sound energy.

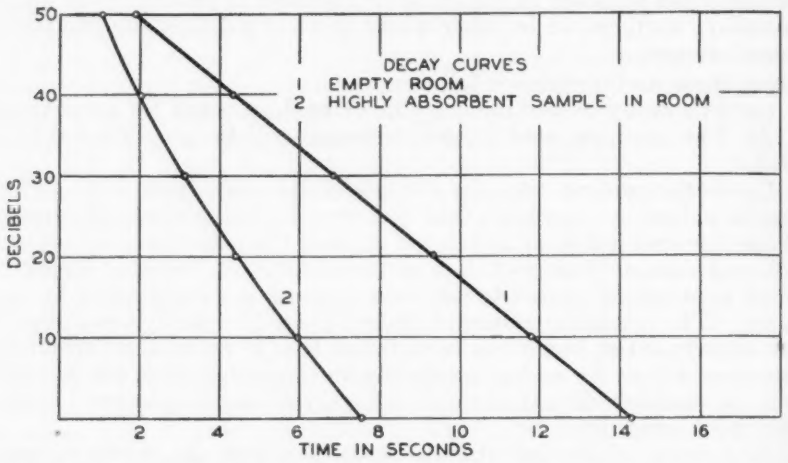

FIGURE 1.—*Curves showing logarithmic decay in empty room and a nonlogarithmic decay when a highly absorbent sample is in the chamber*

It should also be noticed that these vanes are tipped at an angle of approximately 15° from a vertical position. This tends to change sound waves which are traveling in a vertical direction to a horizontal direction and those traveling in a horizontal direction to a vertical. As the vanes rotate this also rotates the sound field about a vertical axis. As a result of these two actions it might be said that the sound field is being rotated about two axes perpendicular to each other, hence a better distribution of sound energy should be obtained.

Figure 3 shows the results obtained after the vanes were installed when a highly absorbent sample of 72 sq ft was again placed in the reverberation chamber. Under these conditions a logarithmic decay of the sound energy was obtained within the experimental error of measurement. As this decay was logarithmic it was assumed that a fairly diffuse distribution of sound energy was obtained by means of the rotating sources and rotating vanes. All of the results given in the rest of the paper are from measurements taken when the vanes were rotating.

[3] The Measurement of Sound Absorption Coefficients by Paul E. Sabine, Journal of the Franklin Institute, 207 (1929).

FIGURE 2.—*Interior of reverberation chamber at National Bureau of Standards.*

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(a) MEASUREMENTS WITH A NONDIRECTIONAL MICROPHONE USING LARGE SAMPLES

It has been known for some time that a satisfactory acoustical treatment cannot be obtained by putting a highly absorbent material only on the ceiling, especially if the ceiling is fairly high. The sound which strikes the highly absorbent material is quickly absorbed but that which strikes the untreated parallel walls is reflected back and forth between these walls and lasts for an appreciably longer time than that between the floor and ceiling. In order to study the decay curves in such a room, enough of each of 3 different kinds of material was obtained to cover the entire floor of the reverberation chamber. The coefficients of these samples are given in table 1. Measurements were made on sample no. 1 at 128, 256, 512, 1,024, 2,048, and 4,096

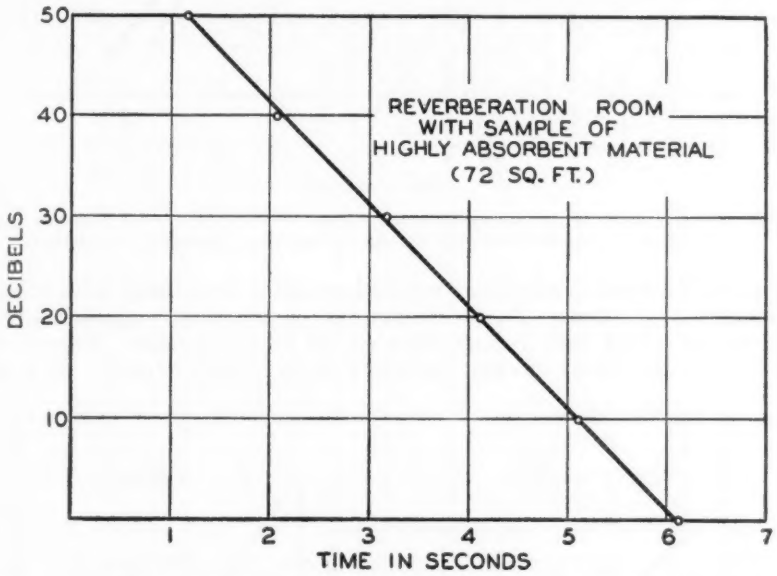

FIGURE 3.—*Curve showing that a logarithmic decay is obtained, when a highly absorbent sample is in the chamber, after rotating vanes are installed*

cycles when approximately one-fourth, one-half, and the whole of the floor was covered. Figure 4 shows the form of decay curves obtained at 512 cycles. In all three cases the decay of sound energy has ceased to be logarithmic, hence it is assumed that there is not a diffuse distribution of sound energy.

The straight lines which are drawn approximately tangent to the upper portions of the curves represent the way the sound should have decayed as computed by the formula. For these computations the coefficient .83 was used, which was the value determined by measurements on a 72 sq ft sample. It should be noticed that the sound starts to decay at the computed rate but the rate becomes smaller and smaller with increased time. The divergence of the measured time from the computed time, which was determined by using the Sabine formula and the coefficient given above, is not greatly different for the three areas. It is important, however, to notice that after a decay of 60 decibels the relative increase in time as measured by the

curve over that indicated by the straight line computed time is quite small for the case where one-quarter of the floor is covered, but when the entire floor is covered this relative increase is approximately 100 percent.

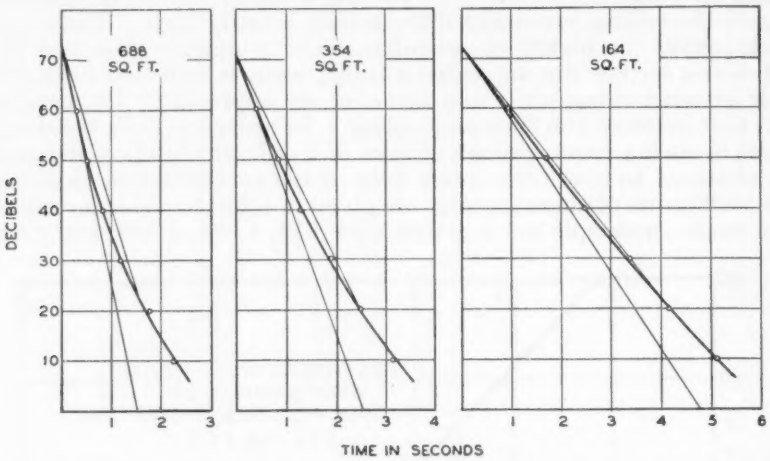

FIGURE 4.—*Decay curves at 512 cycles when approximately all, ½ and ¼ of the floor of the reverberation chamber was covered with sample no. 1 (dynamic microphone)*

The next question was what would happen if a material with a low coefficient were used. To determine this, a material (sample no. 2) was chosen which had a coefficient of .19 at 512 cycles. Figures 5 and 6 show the decay curves, the whole floor being covered. It is to

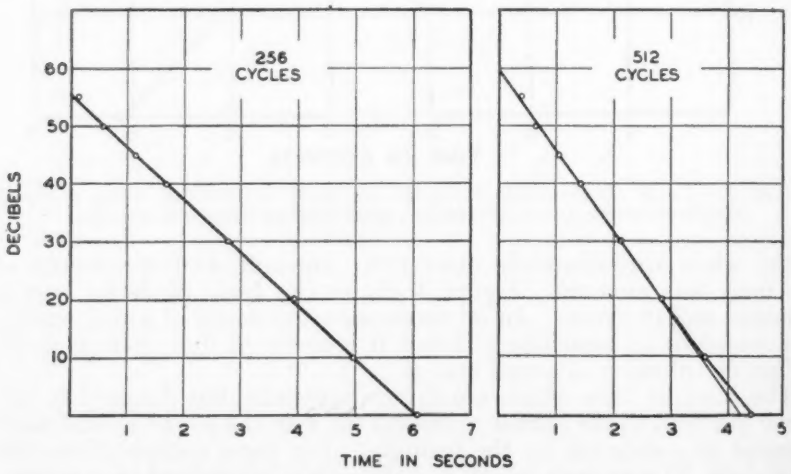

FIGURE 5.—*Decay curves at 256 and 512 cycles when the floor of the reverberation chamber was covered with sample no. 2 (dynamic microphone)*

be noticed that at 256 cycles the decay is logarithmic through the range over which we were able to take measurements. In this case the coefficient of absorption is small, (see table 1) the total absorption being only 79 units. At 512 cycles where the absorption becomes

larger, 137 units, the decay is no longer logarithmic, while at 1,024 and 2,048 cycles, where the absorption is still larger, the divergence from a logarithmic decay is still greater. Figure 7 shows the decay curves at 256 and 512 cycles for sample no. 3, which at these frequencies had absorption coefficients (see table 1) intermediate between these of samples nos. 1 and 2.

From the measurements on these samples it appears that the divergence of the measured rate of decay, caused by placing absorbent material on one surface of a room, is primarily a function of the total amount of absorption and within the error of our measurements was

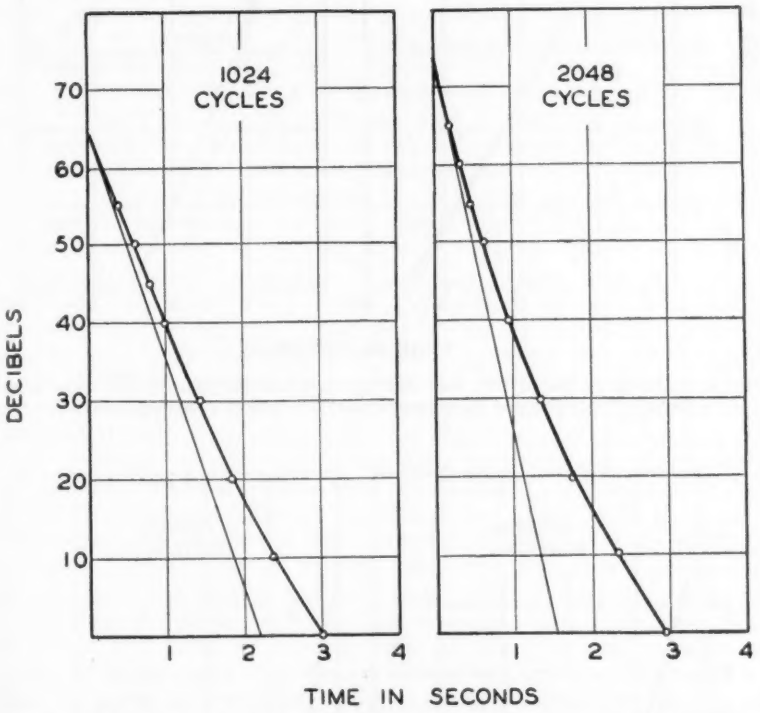

FIGURE 6.—*Decay curves at 1,024 and 2,048 cycles when the floor of the reverberation chamber was covered with sample no. 2 (dynamic microphone)*

independent of the frequency, for frequencies under 2,500 cycles. From these measurements and a large number of others it has been found that when approximately 110 units of absorption are placed on the floor of this reverberation chamber which has an area of 750 sq ft, the sound decay deviates measurably from logarithmic decay, even when a rotating source and rotating vanes are used. In other words, when the total absorption placed on the floor is numerically equal to about one-seventh the area of the floor, a nonlogarithmic decay is obtained. To obtain some idea as to whether this relation was approximately the same in enclosures of a different size similar measurements were made in a 6-ft steel box which was cubical in shape. It was found that about the same ratio between the total absorption and area of surface held as in the reverberation chamber.

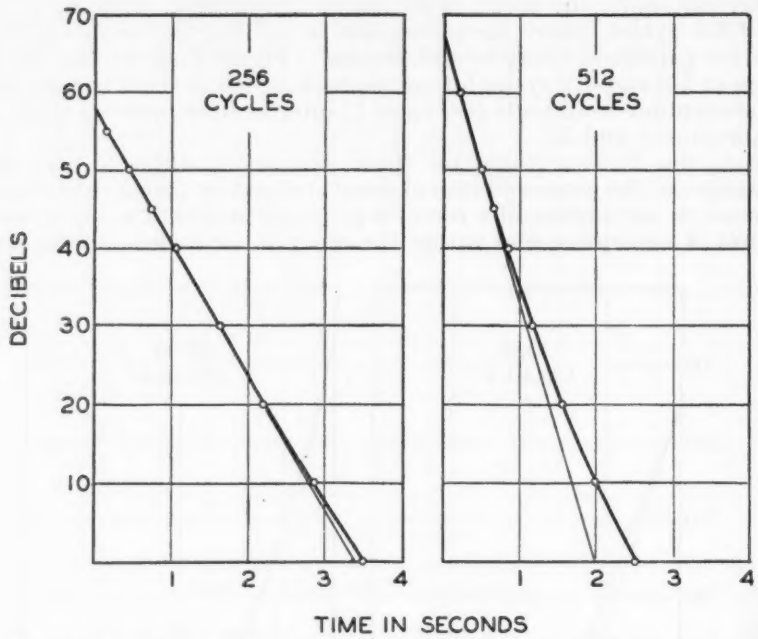

FIGURE 7.—*Decay curves at 256 and 512 cycles when the floor of the reverberation chamber was covered with sample no. 3 (dynamic microphone)*

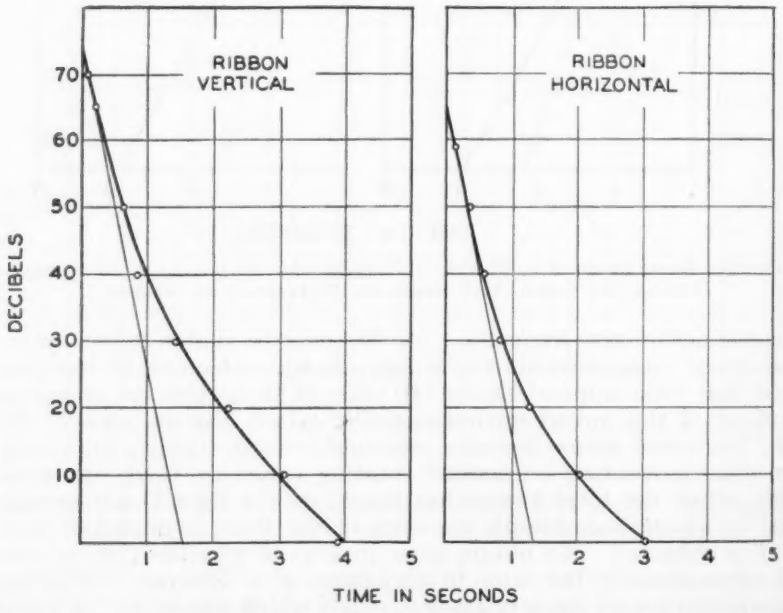

FIGURE 8.—*Decay curves at 512 cycles when the floor of the reverberation chamber was covered with sample no. 1 (ribbon microphone)*

These results might be summarized as follows: When a very small amount of absorption is placed on the floor of the reverberation chamber the decay of sound energy is logarithmic. If this absorption is increased, the decay is still approximately logarithmic for a short time after the sound is cut off, but it becomes less and less so with time. When the entire floor is covered with a highly absorbent material, the decay is not even approximately logarithmic an instant after the loud-speaker is cut off.

(b) MEASUREMENTS WITH A DIRECTIONAL MICROPHONE USING LARGE SAMPLES

All of the measurements given up to the present time were taken with either a condenser or dynamic microphone. Both of these microphones are essentially nondirectional in character. To obtain further evidence as to the distribution of the sound energy it was decided to take some measurements with a microphone, such as a ribbon microphone, which had directional characteristics. Figure 8 shows the results of some of these measurements with practically the whole floor covered with sample no. 1. It will be noticed that the general slopes of the curves are very similar to those taken with the dynamic microphone. There are two important differences in these curves which should be noted. When the ribbon was vertical, the microphone was measuring primarily the sound reflected between the untreated walls. When the ribbon was horizontal, the microphone was measuring primarily the sound reflected between the floor and the ceiling. It will be noticed that the sound level, as indicated by the intersections of these curves with the vertical axis, was higher between the untreated walls than it was between the floor and ceiling, and that the rate of decay was not exactly the same for the two cases. In other words, the measurements show that the distribution of sound flux was markedly different in different directions and that, as in the case of the measurements with the dynamic microphone, the decay is not even nearly logarithmic an instant after the speakers were cut off. Figure 9 shows the results for sample no. 2 at 512 cycles. For this sample, the sound level for 512 cycles was the same in the two directions within the error of measurement at the time the speaker was cut off. Judging from the decay curves a logarithmic decay was maintained approximately for the first 50 or 55 db of the decay, but as the decay continued it became nonlogarithmic.

In the case of the 72 sq ft sample these differences have not been found to exist. The sound level is the same in the two directions and there is a logarithmic decay as with the dynamic microphone.

Table 1 gives the coefficients for the samples as computed from the measurements on an area of 72 sq ft. In addition "absorption coefficients" are given computed from the decay curves obtained when ¼, ½, and the whole of the floor was covered. A chord (see fig. 4) was drawn across the first 50 decibels of the decay curve and the "absorption coefficient" computed on the assumption that the decay had followed this logarithmic curve.

TABLE 1

Area of material	Sound-absorption coefficients for frequencies					
	128	*256*	*512*	*1024*	*2048*	*4096*
SAMPLE NO. 1: DYNAMIC MICROPHONE						
72 square feet area	0.46	0.76	0.83	0.82	0.81	0.78
¼ floor covered (chord)	.42	.68	.67	.69	.77	.75
½ floor covered (chord)		.63	.59	.54	.64	.64
Entire floor covered (chord)		.54	.58	.49	.47	.47
SAMPLE NO. 1: RIBBON MICROPHONE 5 FEET ABOVE FLOOR						
72 square feet area:						
Ribbon vertical			0.81	0.87		
Ribbon horizontal			.82	.85		
Entire floor covered:						
Ribbon vertical (chord)		0.56	.43	.54	0.51	
Ribbon horizontal (chord)		.55	.49	.70	.60	
SAMPLE NO. 2: DYNAMIC MICROPHONE						
72 square feet area		0.10	0.19	0.43	0.73	
Entire floor covered (chord)		.11	.18	.31	.41	
SAMPLE NO. 2: RIBBON MICROPHONE 5 FEET ABOVE FLOOR						
Entire floor covered:						
Ribbon vertical (chord)			0.19	0.33		
Ribbon horizontal (chord)			.19	.38		
SAMPLE NO. 3: DYNAMIC MICROPHONE						
72 square feet area		0.24	0.56	0.65	0.70	
Entire floor covered (chord)		.25	.47	.50	.54	

The foregoing results may partially explain the difference sometimes found between the sound-absorption coefficients obtained by the ear method, which as usually carried out, determines only two points on the decay curve, and those obtained by determining several points on the curve. It is possible that the decay, even under the best conditions, when a highly absorbent sample of 72 sq ft is present in this reverberation chamber, is not logarithmic down to the threshold of the ear, although it is logarithmic within experimental error for the first 70 db. We hope to make further improvements in our equipment so that it will be possible to make measurements at these lower sound intensities which will settle this point.

2. PRACTICAL APPLICATION

It is also desired to call attention to the fact that these curves may aid one in making a better estimate as to what may be expected where there is an acoustical treatment which is applied only on the ceiling. To illustrate this, let us take as an example a room, on which we have measurements, which was 103½ ft long, 23 ft wide, and 13 ft high. In this case all of the acoustical treatment was on the ceiling. Figure 10 shows the decay curves as taken with our measuring equipment using a nondirectional microphone.

Using the formula $T=\frac{.05V}{AS}$ and the coefficients of the different surfaces in the room, the computed reverberation time came out 1.29

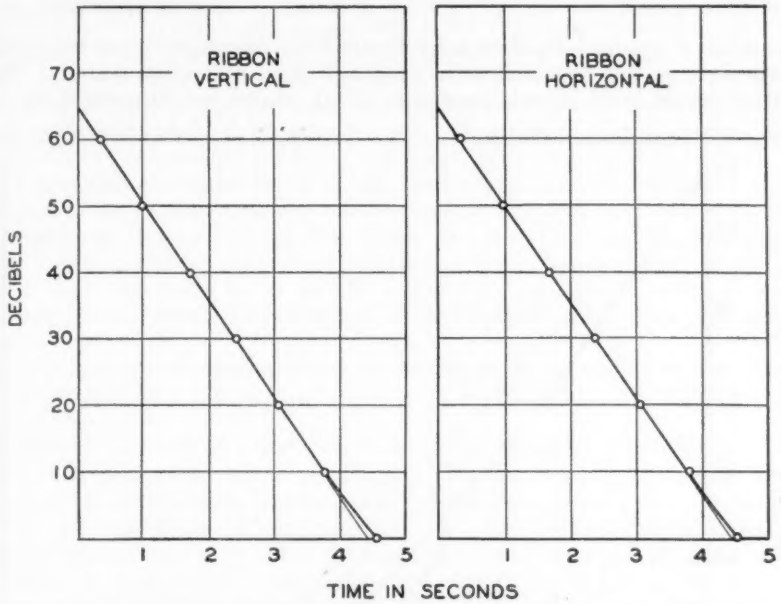

FIGURE 9.—*Decay curves at 512 cycles when the floor of the reverberation chamber was covered with sample no. 2 (ribbon microphone)*

seconds at 512 cycles. This is less than the measured time (1.46 seconds) shown in figure 10. If we make use of the results given in figure 7, in which the sample had approximately the coefficient of

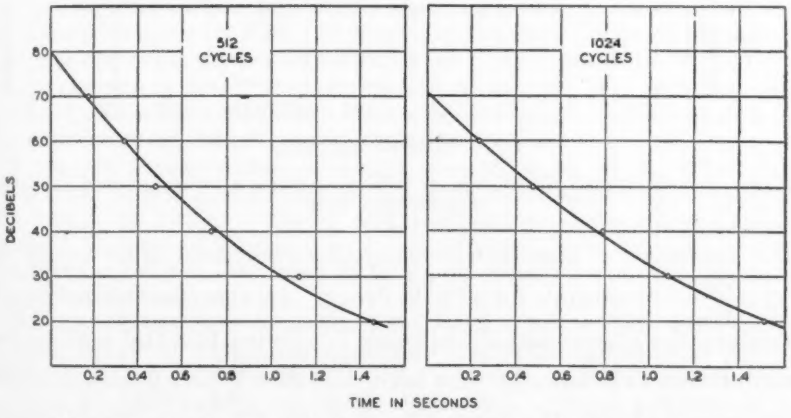

FIGURE 10.—*Decay curves in large room having a ceiling treatment*

the material used as the ceiling treatment in this room, we should be able to estimate approximately the time for a 60 db decay. Referring to figure 7 we find that the time required for a 60 db decay for the

sample was 2.1 seconds at 512 cycles, while if it had decayed logarithmically it should have required only 1.8 seconds. Assuming a similar divergence from a logarithmic decay in the room mentioned above, the time should be $1.29 \times \frac{2.1}{1.8} = 1.5$ seconds. This is approximately the time measured as shown by figure 10. Measurements were also made by the ear method with an organ pipe and stop watch. The initial sound level in this case was 76 db above the threshold of the

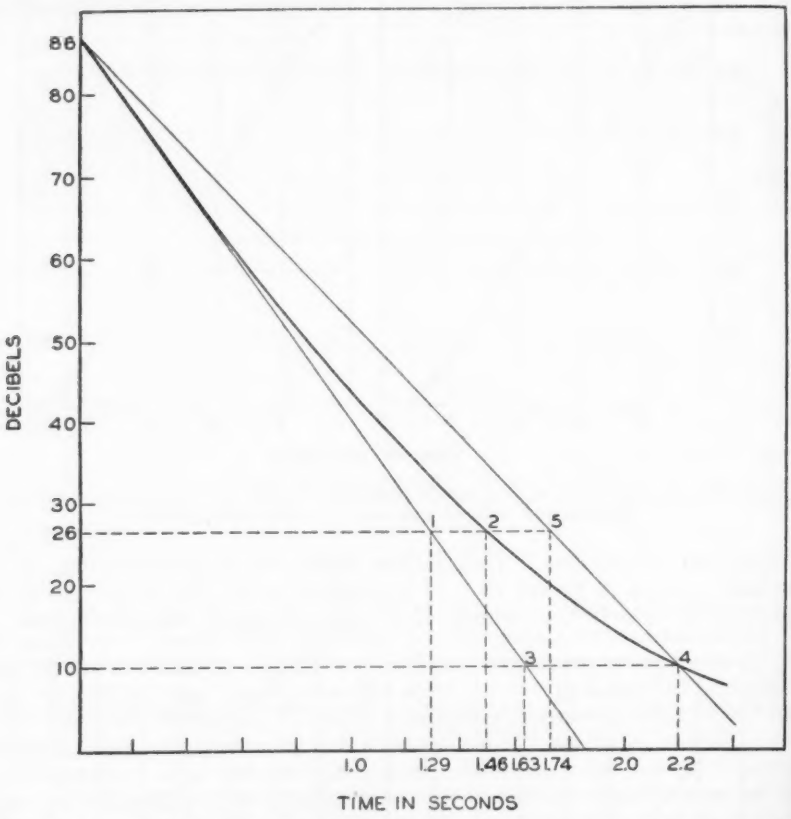

FIGURE 11.—*Graphical illustration of difference between measured and computed reverberation time*

ear. Assuming a logarithmic decay the computed time would be $1.29 \times \frac{76}{60} = 1.63$ seconds for a 76 db decay. In this case it is necessary to extend the curves slightly in figure 7. Doing this and making the computation as before, the time becomes $1.63 \times \frac{3.1}{2.3} = 2.2$ seconds. The time measured with the organ pipe was also 2.2+sec. These results check rather closely, in fact, better than should be expected. Other rooms on which we have made measurements have not checked as well as this one, but at most the error did not exceed .1 of a second. Figure 11 gives a graphical representation of these results. Point (1)

represents the computed time for a 60 db decay. This would also be the correct time if the decay were logarithmic. Point (2) represents the actual time of decay in this room, due to the fact that the decay was not logarithmic. In the same way, point (3) is the computed time for a 76 db decay provided it is logarithmic, point (4) is the actual time for a 76 db decay, and point (5) is the time for a 60 db decay obtained by the ear method using an organ pipe which gave an intensity of 76 db above the ear threshold. It is of interest to note that the time computed by the usual method from the measurement made with this calibrated organ pipe for a 60 db decay is .2 of a second too long, while that computed from the formula is .2 second too small.

In general, the time for a 60 db decay can not be computed correctly by use of the formula, neither can it be measured correctly by determining two points on the decay curve. It is hoped, however, that if enough decay curves are obtained for different types of treatment that the time for a 60 db decay can be approximately close enough for all practical purposes, in some such manner as just indicated.

The above discussion applied primarily to small rooms of less than 30,000 cubic feet. For larger rooms it is probable the divergences are much smaller.

Another case might arise where all of the material is located on the side walls and none on the ceiling. This is entirely different and the curves shown would not apply. Attention should also be called to the fact that these curves apply only to a room which has practically no absorption on the walls. As soon as a small amount of absorbent material is placed on the walls, the decay becomes more nearly logarithmic and the measured time for a 60 db decay approaches that which one would compute from the Sabine formula.

III. EFFECT OF SMALL AREAS

1. EXPERIMENTAL RESULTS

Another problem in measuring absorption coefficients arises from the fact that condition (b), "The absorption of a given material will be proportional to its area" is generally not met although the decay is logarithmic within experimental error. As a result of this, it becomes necessary to choose some size of sample, for reverberation chamber measurements, from which an arbitrary coefficient can be determined which can be used for design purposes.

When the measurement of sound absorption by the reverberation room method was first started at the Bureau of Standards, consideration was given to this problem, and judging from the work of Paul E. Sabine [4] an area of 60 to 70 sq ft was deemed large enough to give satisfactory results. An area of 72 sq ft, or in other words a sample 8 by 9 ft was finally chosen.

During the past few years there has been a race among the various manufacturers of acoustical materials to develop a material having the highest possible absorption. As a result, materials have been developed which have a very high absorption. It was evident, when measurements were made on such materials, that the coefficients computed from measurements on areas of 72 sq ft, were incorrect because in some cases they exceeded 100 percent. It then became

[4] See footnote 3.

necessary to make a further investigation of this problem. To obtain some idea of the effect of area, absorption measurements have been made on different samples of various sizes ranging from 4 sq ft to 144 sq ft. For the smaller areas (4, 9, and 16 sq ft) measurements were first made on a single area. These measurements were repeated many times to eliminate the high probable error of an individual determination caused by the small change in total absorption of the chamber. Later a number of equal small areas were used, giving a

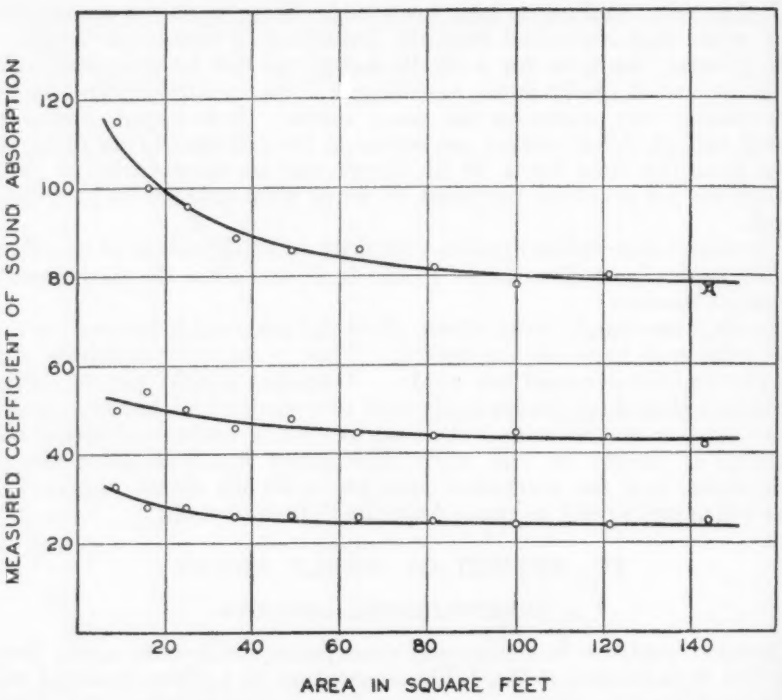

FIGURE 12.—*Variation in measured coefficient with area and magnitude of absorption coefficient at 256 cycles*

total area of 64 or 72 sq ft. In all these cases the areas were separated by more than the width of each (square) area.

The greater total absorption made these determinations easier and the computed absorption coefficients showed no significant difference from the results obtained with a single area. Some of the later measurements on areas of 4, 9, and 16 sq ft were therefore not made on a single area, but by the easier method of several areas. The results of all of these mesaurements on areas varying from 4 to 144 sq ft will be found in figures 12, 13, 14, and 15.

It will be noticed that when the absorption coefficient did not exceed .60, as was the case in the earlier work, the computed coefficient was constant for areas of 72 sq ft and upward so that coefficients determined on samples of this size could be used satisfactorily in computing the effect of larger areas.

For more recent samples with higher absorption, the computed coefficient still decreases with increasing area, at areas greater than

72 sq ft, which would suggest that more satisfactory values of the coefficient would be obtained by using still larger areas. This would be the case were it not for the appearance of nonlogarithmic decay with the larger areas. Figure 16 shows the decay curve for a highly absorbent (coefficient .95) sample of 144 sq ft. The two lower points lie definitely to the right of the straight line. This was the case for all 144 sq ft samples whose computed coefficient was greater than .80. In computing the coefficients in these cases, the slope as indicated by the first four points was used and the last two points ignored. The points marked X on the curves shown in figures 12,

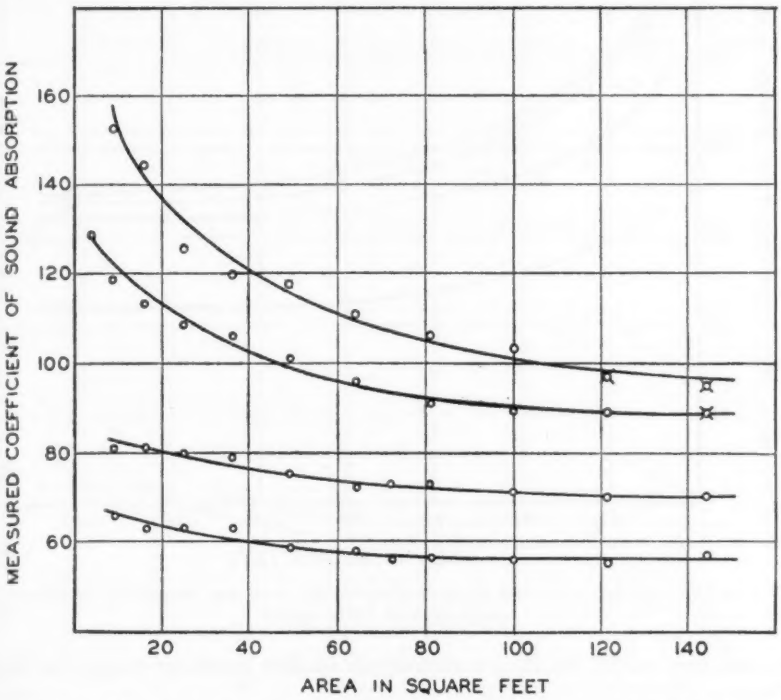

FIGURE 13.—*Variation in measured coefficient with area and magnitude of absorption coefficient at 512 cycles*

13, and 14 were computed from decay curves which showed slight signs of nonlogarithmic decay. In most cases the last point was the only one which deviated from the straight line by an amount greater than the error of measurement. This complication of nonlogarithmic decay as well as the added expense of larger samples made it seem desirable to continue the use of the 72 sq ft area and take account of the affect of area by a correction term.

Examination of the curves of figures 12, 13, 14, and 15 shows that within practical limits, the shape of the curves is independent of the frequency, depending only on the relative absorption. All of the curves are nearly horizontal for areas greater than 120 sq ft, so it seemed reasonable to assume that for sufficiently large areas, providing there was a diffuse distribution of sound energy, the computed coefficients would, even for material with a high absorption, be inde-

pendent of the area. For these cases the curves are sufficiently definite to allow, by extrapolation, a reasonable determination of this limiting value of the absorption coefficient.

In this manner a table of corrections, table 2, has been obtained by which measurements made in the National Bureau of Standards

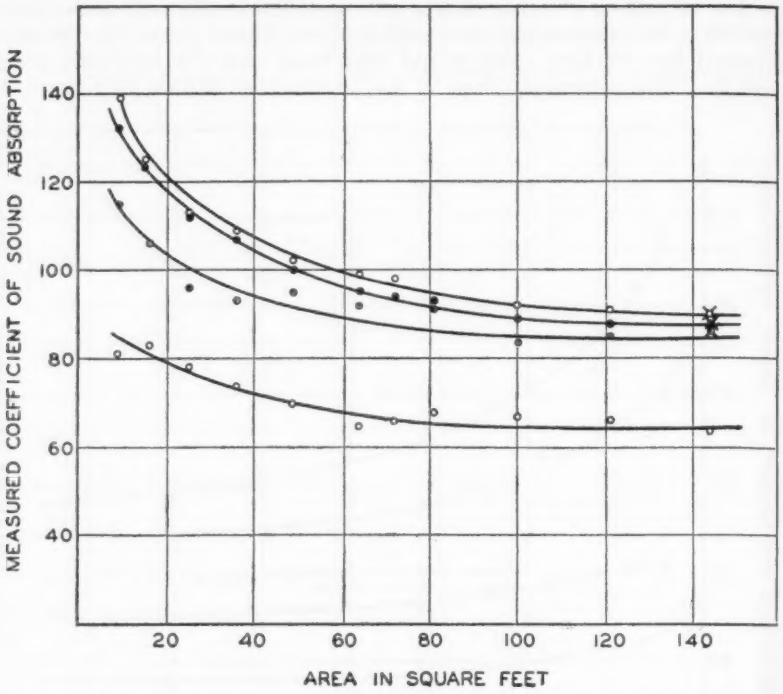

FIGURE 14.—*Variation in measured coefficient with area and magnitude of absorption coefficient at 1,024 cycles*

on samples of 72 sq ft are corrected to the limiting value for large areas.

TABLE 2.—*Correction factors to be subtracted when absorption measurements are made on a sample having an area of 72 square feet*

Measured value for 72 sq ft	Correction	Measured value for 72 sq ft	Correction
1.05	0.09	0.80	0.04
1.00	.07	0.75	.03
0.95	.06	0.70	.02
0.90	.05	0.65	.01
0.85	.05	0.60	.00

There is reason to believe that the above corrections are independent of the room. The basis for this is that we have made a few measurements on a 4 sq ft sample in a 6-ft steel cubical box and find that we obtain the same values as when the measurements are made in the reverberation chamber on the same size of sample.

As far as we know, no one has given a satisfactory explanation why these high absorption values are obtained. It was first suggested that they were due to the absorption of the edges, but in all of the above measurements the edges were covered with angle iron. In view of this fact, the absorption of the edges was very small and this increased absorption must be due to diffraction or some phenomenon of a similar nature.

2. PRACTICAL APPLICATION

There is also a rather important practical application of the results shown in figures 12, 13, 14, and 15. When material is in-

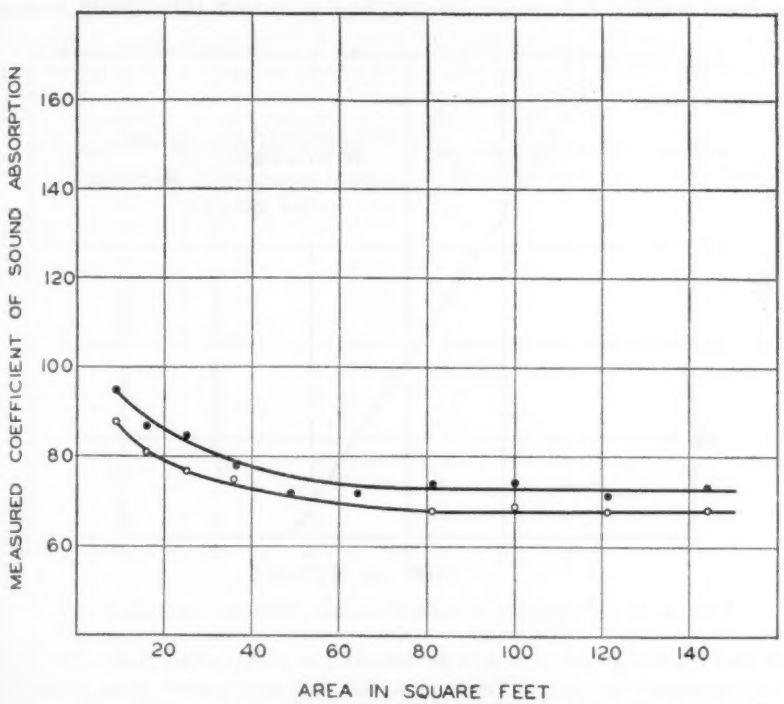

FIGURE 15.—*Variation in measured coefficient with area and magnitude of absorption coefficient at 2,048 cycles*

stalled in small panels the absorption will be greater than indicated by the coefficient. Unless the distance between the panels is sufficient, the increased absorption shown in the above curves will not be obtained. If the distance is too small, the absorption is less and as this distance is further decreased, the absorption is also decreased until finally the absorption becomes that which would be expected from the coefficient when the panels become one continuous area.

We have tested one installation in which the material was in small panels and well distributed, there being four small panels on each wall, each panel having an area of approximately 40 sq ft. The ceiling was coffered, dividing it up into about 250 small squares, each having an area of a trifle over 2 sq ft. Acoustical material having a

coefficient of .95 for a 72 sq ft area, as measured in the reverberation room, was installed in these squares and panels.

From measurements made before and after the installation the average coefficient of sound absorption figures out to be approximately 1.2. At first thought this appears absurd, but if one refers to figure 13 and interpolates for a material having an absorption coefficient of .95 for a 72 sq ft sample, one would get an absorption coefficient of about 1.0 for a 40 sq ft sample and 1.4 for one of 2 sq ft.

As about half the material was installed in the larger panels and the other half in the small squares, this would give 1.2 as the average. It should be realized that it was impossible to make these measurements with a great degree of precision and in checking the results it has been necessary to approximate, but it is very interesting to note

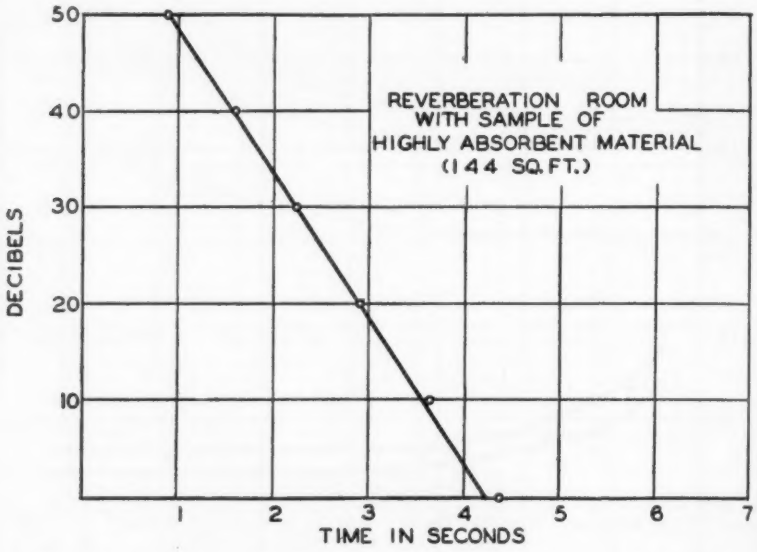

FIGURE 16.—*Beginning of nonlogarithmic decay with increased area*

that the results came out as one would have expected from the laboratory measurements. The reason for this agreement was probably the fact that the distribution of the absorbing material was such that the sound remained in a diffuse condition during the decay.

IV. CONCLUSION

The greatest difficulty in designing a room so that it will be acoustically satisfactory is in determining, in advance of construction, the rate at which the sound energy will decay, as this depends upon the size of the panels of acoustical material and how these panels are distributed on the surfaces of the room. At the present time it is not possible to predict this value accurately, no matter how accurately the coefficient is known. It should be possible, however, if proper studies are made on different types of installations, to establish an empirical relationship so as to obtain the rate of decay accurately enough for all practical purposes.

As additional support to the above statement, we wish to quote from an article by Eyring which was printed in the January 1933 number of the Journal of the Acoustical Society of America:

> Any kind of a reverberation formula used to calculate an absorption coefficient from a reverberation time may be used under the identical circumstances to calculate the reverberation time from the absorption data. In a word, it is simply the process of working forward through a mathematical procedure and then retracing the exact steps to the original data. Therefore, if the identical situation found in a chamber is also found in an auditorium, then any kind of formula could be used with success even though it describes a fictitious physical state.
>
> In practice most reverberation chamber and auditorium situations are not identical. For this reason a reverberation time formula which truly describes the physical reality is much to be desired. In other words a true, not a fictitious, relationship between coefficients of absorption and reverberation time should be determined for as many different situations as possible.

Further work, both experimental and theoretical, is needed to put the computation of the acoustic properties of auditoriums on a satisfactory basis. It is hoped that this paper has indicated some of the directions which such investigations should take.

The author wishes to acknowledge the assistance of Catherine Miller Snyder who made a large part of the experimental observations.

WASHINGTON, June 26, 1934.

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HEATS OF COMBUSTION AND OF FORMATION OF THE NORMAL ALIPHATIC ALCOHOLS IN THE GASEOUS AND LIQUID STATES, AND THE ENERGIES OF THEIR ATOMIC LINKAGES

By Frederick D. Rossini

ABSTRACT

The existing data on the heats of combustion and of vaporization of the normal aliphatic alcohols are correlated with the value recently proposed by the writer for the increase in the heat of combustion per added CH_2 group. Selected "best" values are given for the heats of vaporization at 25 centigrade; for the heats of combustion of the gas and the liquid at 25 centigrade; for the heats of formation from solid carbon and gaseous hydrogen and oxygen at 25 centigrade and at zero Kelvin; and for the heat of the reaction C_nH_{2n+2} (gas) $+\frac{1}{2}$ O_2 (gas) $=$ C_nH_{2n+1} OH (gas) at 25 centigrade and at zero Kelvin.

The energy of dissociation, at the absolute zero, of the normal aliphatic alcohol, C_nH_{2n+1} OH, into its constituent atoms is found to be a linear function of the number of carbon atoms above, but not below, n equal to about 6. The deviations from linearity are in the direction of lesser stability of the molecule and have the following values, in kilocalories per mole: methanol, -3.78 ± 0.10; ethanol, -1.18 ± 0.20; normal propanol, -0.60 ± 0.40; normal butanol, -0.30 ± 0.55; normal pentanol, -0.15 ± 0.70. The deviations can be explained by distinguishing different kinds of C–H, C–C, and C–O linkages in these molecules.

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I. INTRODUCTION

In a previous paper by the writer (1)[1] on the heats of combustion of the gaseous normal paraffin hydrocarbons, the following generalization was made: In any organic molecule containing a normal alkyl group of more than 5 carbon atoms, the addition of a CH_2 group to the normal alkyl radical to form the next higher normal alkyl group results in an increase in the heat of combustion of the organic molecule in the gaseous state, at a temperature of 25 centigrade and a constant total pressure of 1 atmosphere, of 157.00 ± 0.08 k–cal_{15} per mole.

In this paper, the above rule, together with the values obtained in this laboratory for the heats of combustion of methanol and ethanol, is utilized to correlate all the published data on the heats of combustion and of vaporization of the normal aliphatic alcohols, to deduce "best" values for the heats of combustion and of formation of these molecules in the liquid and gaseous states, to compute values for the energies of dissociation of these molecules into their constituent atoms, and to deduce certain relationships concerning the energies of the atomic linkages.

II. UNITS, MOLECULAR WEIGHTS, ETC.

In every case where the distinction is at all significant, the values of energy given in this paper are based upon the international joule as derived from standards maintained at this bureau. As in the previous papers, the following conversion factor[2] is used for reporting the results in calories:

$$1 \text{ international joule} = 1.00040/4.1850 \text{ g–cal}_{15}.$$

The establishment of the uncertainties attached to the various values presented in this paper follows the procedure of the previous papers from this laboratory.

In utilizing the data of those experiments of other investigators where the amount of reaction was determined from the mass of liquid alcohol burned, the value of the heat of combustion per mole was obtained by multiplying the heat of combustion per true gram mass by the molecular weight of the alcohol, computed from the following atomic weights: oxygen, 16.0000; hydrogen, 1.0078; carbon 12.007. The 1934 report of the International Committee on Atomic Weights (3) gives the atomic weight of carbon as 12.00, but there is now little doubt that the true value is greater than this by about 0.05 to 0.08 percent.[3] In this paper, it is necessary to use the value that most nearly represents the atomic weight of carbon, otherwise one is led into the peculiar position of dealing with significantly different sized moles of the same substance. For example, in determining the heat of combustion of hexanol per mole, the amount of reaction in the calorimetric combustion experiments may be determined in three ways: first, from the mass of hexanol divided by its molecular weight; second, from the mass of carbon dioxode formed in the combustion divided by six times the molecular weight of carbon dioxide;

[1] Figures in parentheses here and throughout the text refer to the references at the end of this paper, p. 201.
[2] See p. 736 of reference (2).
[3] See p. 27 of reference (1).

and, third, from the mass of water formed in the reaction divided by seven times the molecular weight of water. If the true atomic weight of carbon is 12.007, then the use of the value 12.00 introduces in the foregoing procedures the following respective errors: first, 0.041 percent; second, 0.016 percent; third, 0.000 percent. In order to obtain the greatest possible accuracy and consistency from the existing data, the value 12.007 is used in this paper for the atomic weight of carbon.

Any accurate measurement of the heat of combustion of an organic compound requires the accurate determination of the amount of reaction per mole of substance burned, from the mass of water or the mass of carbon dioxide formed in the reaction; and if the combustion occurs in a bomb under pressure, then the conditions of the bomb

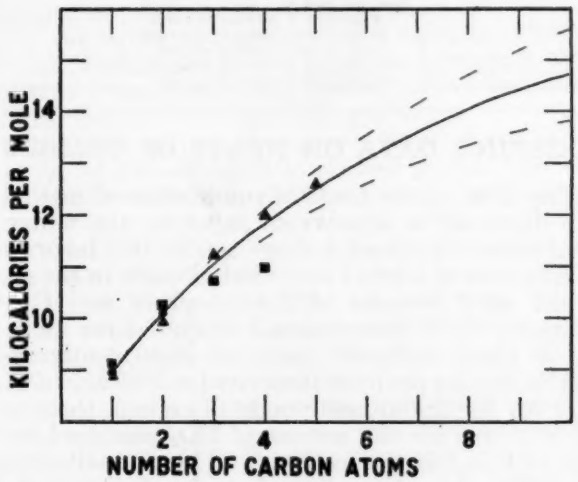


FIGURE 1.—*Plot of the various data on the heats of vaporization of the normal aliphatic alcohols.*

The scale of ordinates gives the heat of vaporization at a temperature of 25 C and at saturation pressure, in k-cal$_{15}$ per mole. The scale of abscissas gives the number of carbon atoms in the normal aliphatic alcohol, $C_nH_{2n+1}OH$. The dashed lines indicate the estimated uncertainty.
The various data are indicated as follows: ●, Fiock, Ginnings, and Holton (7); ■, Bartoszewicz (6); ▲, International Critical Tables (5).

process should be accurately specified in order that the Washburn (4) conversion to 1 atmosphere may be made without error.

III. HEATS OF VAPORIZATION

The existing data on the heats of vaporization of the normal aliphatic alcohols are those given in the International Critical Tables (5) together with the recently reported measurements of Bartoszewicz (6) and of Fiock, Ginnings, and Holton (7).

The various data, corrected to a temperature of 25 C where necessary, are plotted in figure 1. Unplotted values deduced from vapor pressure data have been used to extrapolate the curve to normal decyl alcohol and to estimate the limits of uncertainty. From these and other considerations brought out later in this paper, the writer believes that there must be an error in the values recently reported by

Bartoszewicz (6) for the heats of vaporization of normal propyl and normal butyl alcohols.

From the curve in figure 1, the values given in table 1 have been selected as the "best" values for the heats of vaporization of the normal aliphatic alcohols at saturation pressure and a temperature of 25 C.

TABLE 1.—*Selected "best" values for the heats of vaporization of the normal aliphatic alcohols at saturation pressure and a temperature of 25 C*

Normal $C_nH_{2n+1}OH$	Heat of vaporization at 25 centigrade	Normal $C_nH_{2n+1}OH$	Heat of vaporization at 25 centigrade
	k-cal per mole		*k-cal per mole*
Methanol	8. 94±0. 01	Normal hexanol	13. 05±0. 45
Ethanol	10. 12±0. 02	Normal heptanol	13. 55±0. 55
Normal propanol	11. 05±0. 15	Normal octanol	14. 00±0. 70
Normal butanol	11. 80±0. 25	Normal nonanol	14. 40±0. 85
Normal pentanol	12. 45±0. 35	Normal decanol	14. 70±1. 00

IV. EXISTING DATA ON HEATS OF COMBUSTION

The existing data on the heats of combustion of methyl and ethyl alcohols are discussed in a previous paper by the writer (8). The experimental values obtained 3 years ago in this laboratory for the heats of combustion of methyl and ethyl alcohols in the gaseous state at a constant total pressure of 1 atmosphere are: CH_3OH (gas), at 25 centigrade, 763.68 international kilojoules per mole (measured as 44.000 g of CO_2): C_2H_5OH (gas), at 32.50 centigrade, 1,407.50 international kilojoules per mole (measured as 88.000 g of CO_2). With the value 12.007 for the atomic weight of carbon, there are obtained 44.007 and 88.014 g for the masses of CO_2 produced by 1 mole of CH_3OH and of C_2H_5OH, respectively. This necessitates an increase of 0.016 percent in the values given above for the heats of combustion per mole, which become: CH_3OH (gas), at 25 centigrade, 763.80; C_2H_5OH (gas), at 32.50 centigrade, 1,407.72, international kilojoules per mole at a constant total pressure of 1 atmosphere. Conversion to the standard temperature and to the liquid state yields the following values for the heats of combustion at 25 centigrade and a constant total pressure of 1 atmosphere:

Substance	International kilojoules per mole	$k\text{-cal}_{15}$ per mole
CH_3OH (gas)	763. 80±0. 20	182. 58±0. 05
C_2H_5OH (gas)	1, 408. 83±0. 40	336. 78±0. 10
CH_3OH (liquid)	726. 37±0. 20	173. 64±0. 05
C_2H_5OH (liquid)	1, 366. 51±0. 40	326. 66±0. 10

The following list includes all the investigations which have been published on the heats of combustion of the normal aliphatic alcohols above ethanol: Louguinine (9), propanol; Zubow (10), propanol, butanol, heptanol; Richards and Davis (11), propanol, butanol; Verkade and Coops (12), butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol.

Because of the uncertainty of the conversion of his unit of energy, the data of Louguinine (9) on normal propanol are now only of historical interest.

The data of Zubow (10) were recalculated by Swietoslawski (13). The writer has made the Washburn conversion to 1 atmosphere and converted the values given by Swietoslawski to a temperature of 25 C, obtaining the following values for the heats of combustion of the liquids at a temperature of 25 C and a constant pressure of 1 atmosphere: normal propanol, 480.6 ± 1.2; normal butanol, 638.6 ± 1.6; normal heptanol, $1{,}105.0 \pm 2.8$, k–cal_{15} per mole.

The data of Richards and Davis (11), who did not calibrate their calorimeter electrically, have been converted into the present unit of energy by the use of the factor which makes their value for ethanol identical with that obtained by the writer 3 years ago (8). Following this procedure, the writer obtains from their data the following values for the heats of combustion of the liquid at a temperature of 25 C and at a constant pressure of 1 atmosphere: normal propanol, 482.1 ± 0.6; normal butanol, 637.7 ± 0.8, k–cal_{15} per mole.

Verkade and Coops (12) made a careful study of the heats of combustion of the liquid normal aliphatic alcohols from butanol to decanol. These investigators calibrated their calorimeter with benzoic acid, operating at a temperature of 19.5 C and using in their bomb an initial oxygen pressure of 35 atmospheres. For the heat of combustion of benzoic acid in the bomb calorimeter under these conditions, Verkade and Coops used the value 6,324.0 cal_{15} per gram weighed in air, which is equivalent to 6,318.9 cal_{15} per true gram mass. From recent experiments at this bureau, Jessup (14) has found the heat of combustion of benzoic acid in a bomb calorimeter at a temperature of 25 C to be 26,419 international joules per true gram mass, under the standard conditions (of the bomb process) proposed by Washburn (4). For the conditions of the experiments of Verkade and Coops, Jessup's value becomes 26,427 international joules, or, using the factor 1.00040/4.1850, 6,317.2 cal_{15} per true gram mass of benzoic acid. The Washburn correction to 1 atmosphere which must be applied to these data of Verkade and Coops is computed to be -0.035 percent. On conversion to a temperature of 25 C, the data of Verkade and Coops yield the following values for the heat of the reaction,

$$C_nH_{2n+1}OH \text{ (liquid)} + \frac{3n}{2} O_2 \text{ (gas)} = nCO_2 \text{ (gas)} + (n+1) H_2O \text{ (liquid)}, \quad (1)$$

at a temperature of 25 C and a constant pressure of 1 atmosphere, in k–cal_{15} per mole: normal butanol, 638.93 ± 0.38; normal pentanol, 794.89 ± 0.48; normal hexanol, 951.05 ± 0.57; normal heptanol, $1{,}107.51 \pm 0.66$; normal octanol, $1{,}263.96 \pm 0.76$; normal nonanol, $1{,}419.79 \pm 0.85$; normal decanol, $1{,}575.60 \pm 0.95$.

V. SELECTED VALUES FOR THE HEATS OF COMBUSTION OF THE ALCOHOLS IN THE LIQUID STATE

The various values given in the foregoing section are plotted in figure 2, in terms of the function $(Qc - 12.00)/n$, where Qc is the heat of reaction (1) in k–cal_{15} per mole, n is the number of carbon atoms in the molecule, and the constant 12.00, chosen arbitrarily, is used in

order to obtain a compact plot of the values. From the curve in this plot, the values given in table 2 have been selected as the "best" values for the heat evolved in reaction (1) at a temperature of 25 C and a constant pressure of 1 atmosphere.

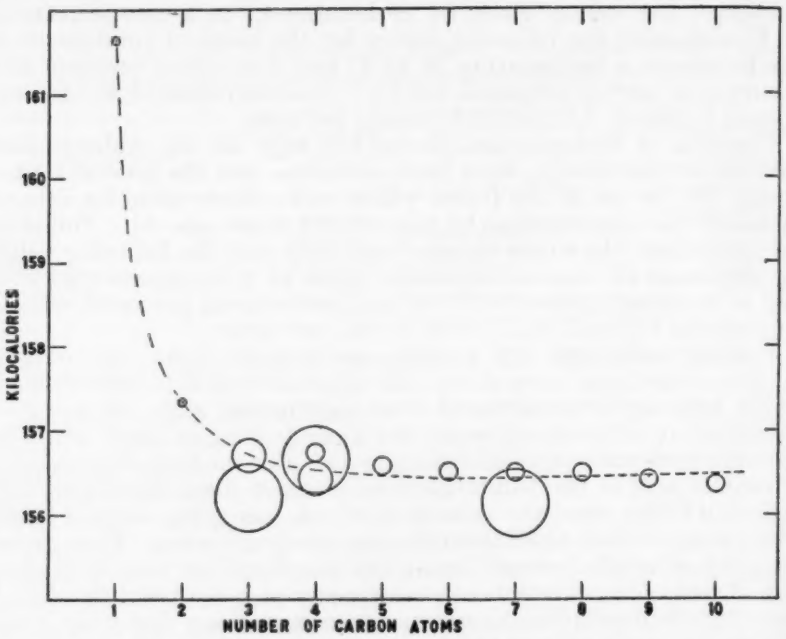


FIGURE 2.—*Plot of the various data on the heats of combustion of the normal aliphatic alcohols in the liquid state.*

The scale of ordinates gives the function $(Qc-12.00)/n$, in k-cal$_{15}$ per carbon atom, where Qc is the heat of combustion of the liquid, in k-cal$_{15}$ per mole, at 25 centigrade and a constant pressure of 1 atmosphere. The scale of abscissas gives n, the number of carbon atoms in the molecule. The circles are drawn with radii equal to the estimated uncertainties in the various values, the sources of which are given in the text.

TABLE 2.—*Selected "best" values for the heats of combustion of the normal aliphatic alcohols in the liquid state at a temperature of 25 C and a constant pressure of 1 atmosphere*

$$[C_nH_{2n+1}OH\,(\text{liquid})+\frac{3n}{2}O_2(\text{gas})=nCO_2(\text{gas})+(n+1)\,H_2O\,(\text{liquid})]$$

Normal $C_nH_{2n+1}OH$ (liquid)	Heat of combustion at 25 centigrade and constant pressure	Normal $C_nH_{2n+1}OH$ (liquid)	Heat of combustion at 25 centigrade and constant pressure
	k-cal$_{15}$ per mole		*k-cal$_{15}$ per mole*
Methanol	173.64±0.05	Normal hexanol	950.55±0.48
Ethanol	326.66±0.10	Normal heptanol	1,107.05±0.56
Normal propanol	482.15±0.24	Normal octanol	1,263.60±0.64
Normal butanol	638.10±0.32	Normal nonanol	1,420.20±0.72
Normal pentanol	794.30±0.40	Normal decanol	1,576.90±0.80

VI. SELECTED VALUES FOR THE HEATS OF COMBUSTION OF THE ALCOHOLS IN THE GASEOUS STATE

Combination of the selected "best" values for the heats of combustion of the normal aliphatic alcohols in the liquid state with the selected "best" values for the heats of vaporization yields selected "best" values for the heats of combustion of the alcohols in the gaseous state according to the reaction,

$$C_nH_{2n+1}OH \text{ (gas)} + \tfrac{3n}{2}O_2\text{(gas)} = nCO_2 \text{ (gas)} + (n+1)\ H_2O \text{ (liquid)}, \quad (2)$$

at a temperature of 25 C and a constant total pressure of 1 atmosphere. These values are given in table 3 and are plotted in figure 3.

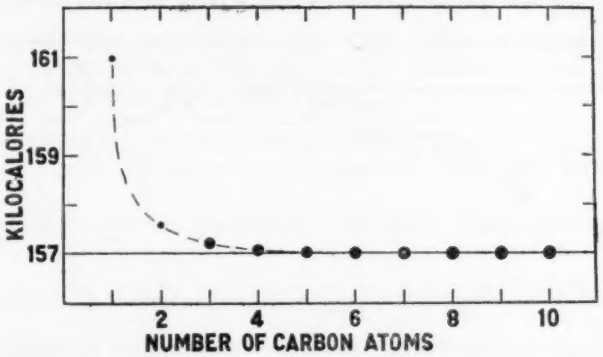


FIGURE 3.—*Plot of the selected "best" values for the heats of combustion of the normal aliphatic alcohols in the gaseous state.*

The scale of ordinates gives the function $(Qc-21.60)/n$, in k-cal$_{15}$ per carbon atom, where Qc is the heat of combustion of the gas, in k-cal$_{15}$ per mole, at 25 centigrade and a constant total pressure of 1 atmosphere. The scale of abscissas gives n, the number of carbon atoms in the molecule. The circles are drawn with radii equal to the estimated uncertainties.

TABLE 3.—*Selected "best" values for the heats of combustion of the normal aliphatic alcohols in the gaseous state at a temperature of 25 C and a constant total pressure of 1 atmosphere*

$$[C_nH_{2n+1}OH \text{ (gas)} + \tfrac{3n}{2}O_2 \text{ (gas)} = nCO_2 \text{ (gas)} + (n+1)\ H_2O \text{ (liquid)}]$$

Normal $C_nH_{2n+1}OH$ (gas)	Heat of combustion at 25 centigrade and constant pressure	Normal $C_nH_{2n+1}OH$ (gas)	Heat of combustion at 25 centigrade and constant pressure
	k-cal$_{15}$ per mole		*k-cal$_{15}$ per mole*
Methanol	182.58±0.05	Normal heptanol	1,120.60±0.78
Ethanol	336.78±0.10	Normal octanol	1,277.60±0.94
Normal propanol	493.20±0.28	Normal nonanol	1,434.60±1.11
Normal butanol	649.90±0.40	Normal decanol	1,591.60±1.28
Normal pentanol	806.75±0.53	Normal $C_nH_{2n+1}OH$, $n>5$	$21.60+n(157.00\pm0.12)$
Normal hexanol	963.60±0.66		

The values of the heats of combustion of the gaseous normal aliphatic alcohols are a linear function of n above, but not below, n equal to about 6. The deviations from linearity are in the direction of greater values of the heats of combustion, and are, in kilocalories per mole: methanol, 3.98 ± 0.05; ethanol, 1.18 ± 0.10; normal propanol, 0.60 ± 0.28; normal butanol, 0.30 ± 0.40; normal pentanol, 0.15 ± 0.53.

VII. CHANGE IN HEAT CONTENT, AT 25 CENTIGRADE AND AT ZERO KELVIN, FOR THE REACTION OF ADDING $\frac{1}{2}$ O_2 TO A NORMAL PARAFFIN HYDROCARBON TO FORM THE CORRESPONDING NORMAL ALIPHATIC ALCOHOL

The difference in the heats of combustion of the gaseous normal paraffin hydrocarbons and their analogous gaseous normal aliphatic alcohols yields the change in heat content for the process of adding $\frac{1}{2}$ O_2 (gas) to normal C_nH_{2n+2} (gas) to form normal $C_nH_{2n+1}OH$ (gas):

$$C_nH_{2n+2}\ (\text{gas}) + \tfrac{1}{2}O_2\ (\text{gas}) = C_nH_{2n+1}OH\ (\text{gas}) \qquad (3)$$

Using for the heats of combustion of the gaseous normal paraffin hydrocarbons the values given by the writer in a previous paper (1),

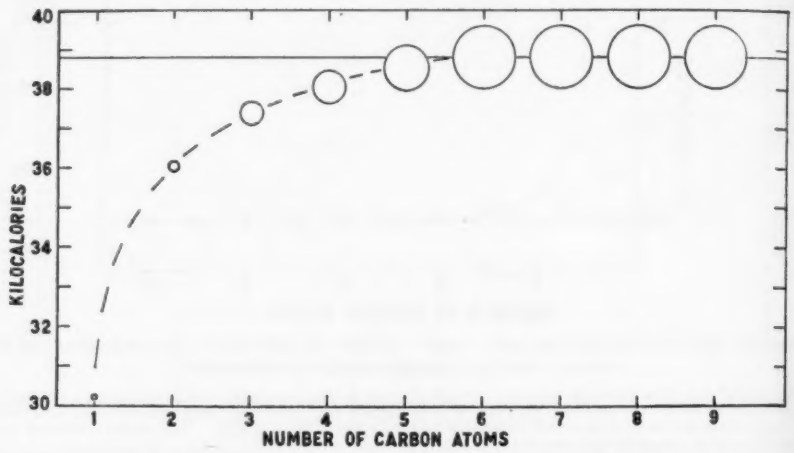


FIGURE 4.—*Plot of the values for the heat of the reaction of adding $^1/_2O_2$ to a normal paraffin hydrocarbon to form the corresponding normal aliphatic alcohol.*

The scale of ordinates gives the heat evolved in the reaction, *normal* $C_nH_{2n+2}(gas)+1/2\ O_2(gas) = normal\ C_nH_{2n+1}OH(gas)$, at 25 centigrade and a constant total pressure of 1 atmosphere, in k-cal$_{15}$ per mole. The scale of abscissas gives the number of carbon atoms in the molecule. The circles are drawn with radii equal to the estimated uncertainties.

and for the heats of combustion of the normal aliphatic alcohols the values given in table 3 of this paper, the writer obtains the values given in table 4 for the change in heat content for reaction 3 at a temperature of 25 C and a constant total pressure of 1 atmosphere. These values are plotted in figure 4.

TABLE 4.—*The change in heat content, at 25 centigrade and at zero Kelvin, for the reaction of adding $\frac{1}{2}$ O_2 to a normal paraffin hydrocarbon to form the corresponding normal aliphatic alcohol*

$[C_nH_{2n+2}\ (\text{gas}) + 1/2\ O_2\ (\text{gas}) = C_nH_{2n+1}OH\ (\text{gas})]$

n	$\Delta H°_{298.1}$	$\Delta H°_0$
	k-cal 15 per mole	*k-cal 15 per mole*
1	−30.21±0.08	−29.98±0.13
2	−36.03±0.15	−35.80±0.18
3	−37.37±0.30	−37.14±0.32
4	−38.04±0.43	−37.81±0.45
5	−38.52±0.57	−38.29±0.59
6	−38.80±0.82	−38.57±0.84
$n>5$	−38.80±0.82	−38.57±0.84

In order to compute the change in heat content for reaction 3 at zero Kelvin, there are required values of the quantity $H^\circ_{298.1} - H^\circ_0$ for normal C_nH_{2n+2} (gas), O_2 (gas), and normal $C_nH_{2n+1}OH$ (gas). Values for the first two substances are given in the previous paper (1). There have not been published any calculations of this quantity for the gaseous normal aliphatic alcohols; but the writer estimates, from the published meager data on the difference in the heat capacities of methane and methanol and of ethane and ethanol, that the value of $H^\circ_{298.1} - H^\circ_0$ for normal $C_nH_{2n+1}OH$ (gas) is greater than that for the corresponding normal paraffin hydrocarbon by about 0.80 ± 0.10 k–cal per mole.

Hence for reaction 3,

$\Delta H^\circ_0 = \Delta H^\circ_{298.1} - (0.70 \pm 0.10)$ k–cal_{15} per mole (4).

The values so obtained are given in table 4.

VIII. HEATS OF FORMATION OF THE NORMAL ALIPHATIC ALCOHOLS FROM SOLID CARBON AND GASEOUS HYDROGEN AND OXYGEN

Combination of the values given in tables 1 and 4 of this paper with those given in table 2 of the previous paper (1) yields for the reactions,

$$C\ (\beta\ \text{graphite}) + (n+1)\ H_2\ (\text{gas}) + \tfrac{1}{2}\ O_2\ (\text{gas}) = C_nH_{2n+1}OH\ (\text{gas}) \quad (5)$$

and

$$C\ (\text{diamond}) + (n+1)\ H_2\ (\text{gas}) + \tfrac{1}{2}\ O_2\ (\text{gas}) = C_nH_{2n+1}OH\ (\text{gas}), \quad (6)$$

at temperatures of 25 C and zero Kelvin and a constant total pressure of 1 atmosphere, the values given in table 5. There are also included in table 5 values for the analogous formation of the normal aliphatic alcohols in the liquid state at a temperature of 25 C.

TABLE 5.—*Heats of formation, at 25 centigrade and zero Kelvin, of the normal aliphatic alcohols from solid carbon and gaseous hydrogen and oxygen*

C (solid)+$(n+1)H_2$(gas)+1/$2O_2$(gas)=$C_nH_{2n+1}OH$(gas, or liquid)

Normal $C_nH_{2n+1}OH$	To form normal $C_nH_{2n+1}OH$ (gas)				To form normal $C_nH_{2n+1}OH$ (liquid)			
	From C (β graphite)		From C (diamond)		From C (β graphite)		From C (diamond)	
	$\Delta H°_{298.1}$	ΔH_0	$\Delta H°_{298.1}$	ΔH_0	$\Delta H°_{298.1}$		$\Delta H°_{298.1}$	
	k-cal$_{15}$ *per mole*	*k-cal*$_{15}$ *per mole*	*k-cal*$_{15}$ *per mole*	*k-cal*$_{15}$ *per mole*	*k-cal*$_{15}$ *per mole*		*k-cal*$_{15}$ *per mole*	
Methanol	−48.28±0.10	−46.16±0.14	−48.50±0.10	−46.51±0.14	−57.22±0.10		−57.44±0.10	
Ethanol	−56.63±0.22	−52.79±0.25	−57.07±0.22	−53.49±0.25	−66.75±0.22		−67.19±0.22	
Normal propanol	−62.76±0.40	−57.41±0.45	−63.42±0.40	−58.46±0.45	−73.81±0.36		−74.47±0.36	
Normal butanol	−68.61±0.57	−61.74±0.60	−69.49±0.57	−63.14±0.60	−80.41±0.48		−81.29±0.48	
Normal pentanol	−74.51±0.73	−65.93±0.80	−75.41±0.73	−67.68±0.80	−86.76±0.60		−87.86±0.60	
Normal hexanol	−80.01±0.85	−70.09±0.97	−81.33±0.85	−72.19±0.97	−93.06±0.72		−94.38±0.72	
Normal heptanol	−85.56±1.00	−74.12±1.15	−87.10±1.00	−76.57±1.15	−99.11±0.84		−100.65±0.84	
Normal octanol	−91.11±1.18	−78.15±1.33	−92.87±1.18	−80.95±1.33	−105.11±0.96		−106.87±0.96	
Normal nonanol	−96.66±1.37	−82.18±1.51	−98.64±1.37	−85.33±1.51	−111.06±1.08		−113.04±1.08	
Normal decanol	−102.21±1.56	−86.21±1.70	−104.41±1.56	−89.71±1.70	−116.91±1.20		−119.11±1.20	
Normal $C_nH_{2n+1}OH$, $n>5$	$-46.71-n(5.55\pm0.15)$	$-45.91-n(4.03\pm0.17)$	$-46.71-n(5.77\pm0.15)$	$-45.91-n(4.38\pm0.17)$				

IX. ENERGY OF DISSOCIATION OF NORMAL $C_nH_{2n+1}OH$ INTO GASEOUS ATOMS, AND THE ENERGIES OF THE ATOMIC LINKAGES

The energy absorbed at the absolute zero in the reaction of dissociating the gaseous molecule $C_nH_{2n+1}OH$ (normal aliphatic alcohol), into its constituent gaseous atoms, each in the normal state,

$$C_nH_{2n+1}OH\ (gas) = nC\ (gas) + (2n+2)H\ (gas) + O\ (gas), \qquad (7)$$

is given by the expression,

$$(Da)^\circ_\circ = -Qc_{298.1} + n(132.880 \pm 0.032) + (65.256 \pm 0.010) + nD_{CO} + (n+1)D_{H_2} - \frac{n-1}{2}D_{O_2} + (H^\circ_{298.1} - H^\circ_\circ)\ [\text{alcohol}], \qquad (8)$$

where $Qc_{298.1}$ is the heat evolved in the combustion of the normal aliphatic alcohol according to reaction (2), D_{CO}, D_{H_2}, and D_{O_2} are the

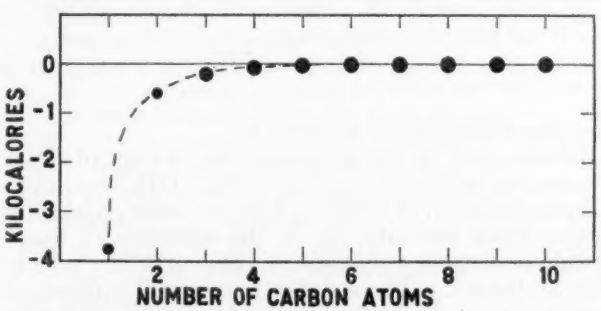


FIGURE 5.—*Plot of the deviations from linearity in the relation between the number of carbon atoms in the normal aliphatic molecule and its energy of dissociation into atoms.*

The scale of ordinates gives Δ, the deviation from linearity in the relation between n and the energy of dissociation at zero Kelvin, according to the reaction, $C_nH_{2n+1}OH(gas) = nC(gas) + (2n+2)H(gas) + O(gas)$, in kilocalories per carbon atom. The scale of abscissas gives n, the number of carbon atoms in the molecule. The circles are drawn with radii equal to the estimated uncertainties.

energies absorbed at the absolute zero in the reaction of dissociating the molecules CO, H_2 and O_2, in the normal state, into their constituent atoms, each in the normal state, and the last term is the heat content of the gaseous normal aliphatic alcohol at 298.1 Kelvin minus its heat content at zero Kelvin. For the values of $H^\circ_{298.1} - H^\circ_\circ$ for the gaseous normal aliphatic alcohols, the writer takes the following values (see preceding section): Methanol, 3.20 ± 0.10; $n > 1$, $(2.25 \pm 0.10) + 0.75n(1 \pm 0.01n)$, k–cal per mole.

By means of equation 8 and the values given here, the writer has computed the values for Δ, the deviation from linearity in the relation between $(Da)^\circ_\circ$ and n, which are given in table 6 and plotted in figure 5.

TABLE 6.—*Deviations from linearity with n in the energy of dissociation, at the absolute zero, of the normal aliphatic alcohols into their constituent atoms*

Normal $C_nH_{2n+1}OH$ (gas)	Δ	
	k-cal per mole	*k-cal per carbon-atom*
Methanol	−3.78±0.10	−3.78±0.10
Ethanol	−1.18±0.20	−0.59±0.10
Normal propanol	−0.60±0.40	−0.20±0.13
Normal butanol	−0.30±0.55	−0.08±0.14
Normal pentanol	−0.15±0.70	−0.03±0.14
Normal $C_nH_{2n+1}OH$, $n>5$	0.00±0.14n	0.00±0.14

For any of the normal aliphatic alcohols, the energy of reaction,

$$C_nH_{2n+1}OH\ (gas) = nC(gas) + (2n+2)H\ (gas) + O\ (gas), \qquad (7)$$

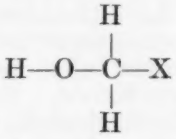
when all the substances are in their normal states at the absolute zero of temperature, is given by the equation

$$(Da)^\circ_0 = (45.91 \pm 0.10) - n(23.37 \pm 0.14) + nD_{CO} + (n+1)D_{H_2} - \frac{n-1}{2}D_{O_2} + \Delta\ \text{k-cal}_{15}\ \text{per mole}, \qquad (9)$$

where Δ has the values given in table 6.

Within the accuracy of these values, the energy of dissociation of the gaseous normal aliphatic alcohol, $C_nH_{2n+1}OH$, into its constituent atoms is a linear function of n above, but not below, n equal to about 6. The deviations from linearity are in the direction of lesser stability of the molecule and reach a maximum value of 3.78 ± 0.10 kilocalories per mole for methanol. These deviations are of opposite sign from, and have values about ⅔ of, those found for the corresponding normal paraffin hydrocarbons.

In a manner similar to that used by the writer in the case of the normal paraffin hydrocarbons (1), the above deviations can be explained by assuming different kinds of C–C, C–H, and C–O linkages in the normal aliphatic alcohols. For example, one can distinguish two kinds of C–H linkages and two kinds of C–O linkages in the molecule



a_4 is the C–H linkage when X = H,

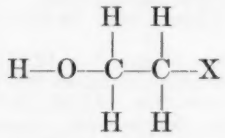
a_5 is the C–H linkage when X = R (a normal alkyl radical),

d_1 is the C–O linkage when X = H,

d_2 is the C–O linkage when X = R, and

c_1 is the O–H linkage.

Similarly, one can distinguish two kinds of C–C linkages in the molecule



b_{10} is the C–C linkage when X = H and
b_{11} is the C–C linkage when X = R.

On this basis the energies of the atomic linkages in the normal aliphatic alcohols can be represented as follows:

Methanol	$c_1+d_1+3a_4$
Ethanol	$c_1+d_2+2a_5+3a_1+b_{10}$
Normal $C_nH_{2n+1}OH$, $(n>2)$	$c_1+d_2+2a_5+3a_1+b_{10}+b_{11}+2(n-2)a_2+(n-3)b_2$.

The successive differences become constant and equal to $2a_2+b_2$ above $n=3$. This approximates what the experimental data indicate, but (as previously pointed out in the case of the normal paraffin hydrocarbons) in a more exact sense one would need to distinguish between various normal alkyl radicals designated by R in the above notation.

Whereas, for the series of normal paraffin hydrocarbons the positive deviations from linearity in going from hexane to methane could be attributed in large part to the fact that the strengths of the C–H linkages are in the increasing order a_2, a_1, a_0; for the series of normal aliphatic alcohols the negative deviations from linearity in going from hexanol to methanol can be explained in large part by assuming that the strengths of the C–O linkages are in the decreasing order d_2, d_1.

Within the accuracy of the present values, each atom in the molecule may be said to have a sphere of influence, with regard to energy, that includes the atoms twice removed from it.

Any assignment of values for the energies of the various linkages in the normal aliphatic molecule, $C_nH_{2n+1}OH$, must satisfy the following relation:

$$\Sigma m_i l_i=(Da)^0_0+nE_e \qquad (10)$$

Here l_i is the value assigned to represent the energy of each atomic linkage of the kind i, the number of which is m_i; E_e is the energy of excitation of the carbon atom to the excited tetravalent ^5S state; n is the number of carbon atoms in the molecule; and $(Da)^0_0$ is given by equation 9.

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WASHINGTON, June 13, 1934.

U.S. Department of Commerce, National Bureau of Standards

RESEARCH PAPER RP702

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August 1934

A BRIGHTNESS METER FOR LUMINOUS PREPARATIONS

By L. F. Curtiss

ABSTRACT

A small portable brightness meter built on the principle described by Crawford, J.Sci.Inst. 11,14(1934); has been designed for determining the brightness of luminous preparations. The instrument measures brightnesses from 2 to 75 μL, using a milliammeter with a full scale reading of 10 ma. Operated from 2 dry cells, the apparatus is entirely self-contained.

I. INTRODUCTION

Tests of samples of luminous material for brightness are usually made with the luminous powder in the dry state. These samples are most frequently in the form of stoppered glass tubes, 5 to 8 mm in diameter containing a gram or so of the powder. The brightness of these preparations ranges from 5 to 30 μL. To cover this range by the method of varying the brightness of a comparison screen by changing the distance of a standard lamp on a track requires a track about 2 m long and the apparatus occupies considerable space. This note describes an application to this problem of the brightness meter developed by Crawford.[1] This results in an instrument of small size and weight which is convenient to use and is readily portable.

II. DESCRIPTION OF INSTRUMENT

In the instrument designed by Crawford the variation of brightness is produced by changing the current through a lamp which is placed in 1 arm of a wheatstone bridge circuit, the other 3 arms of which have fixed resistances. A milliammeter connected between the balance points of the bridge reads the out-of-balance current of the bridge due to changes of resistance of the lamp as the applied voltage is changed. In applying this arrangement to the problem under dis-

[1] Crawford, B. H., J.Sci.Inst., 11,14 (1934).

cussion it is necessary to determine a combination of resistances, which will give suitable readings on a milliammeter to cover the range of brightnesses involved. An additional factor is the color filter required to correct the color of the comparison surface to agree with that of the luminous preparation.

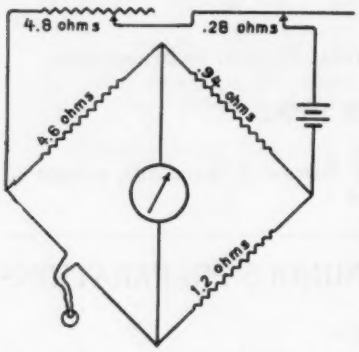

FIGURE 1.—*Wiring diagram of wheatstone bridge circuit.*

As the actual selection of values for these components is somewhat more difficult than might appear from a casual consideration, complete details are given of the arrangement which has been found to be satisfactory. This should render the duplication of the apparatus possible with only slight adjustments of the fixed resistances.

Although the departures from Crawford's arrangement are of a minor nature, they entail the use of quite different values of resistances and voltage as well as the use of a meter of lower sensitivity. The problem was approached by first choosing a lamp and color filter. Since they are always readily available, a 3-cell flashlight lamp (trade number 13) was selected. This also makes it possible to operate the device from dry cells or even flashlight cells, so that it will be readily portable. The resistances which were found to give suitable deflections when a 10-ma meter was used and the voltage supplied by 2 dry cells are recorded in the diagram, figure 1, which shows the complete electrical circuit of the instrument.

The color filter used was made up of a piece of opal glass about 1 mm thick and a piece of a Corning green railway-signal roundel having a transmission of approximately 140 percent on the American Railway Association scale. This combination gave a brightness of the opal glass of about 2 μL/ft-c on the green side of the filter.

The relative positions of the photometer cube, lamp, filter, and luminous preparation are shown in figure 2. The glass tube containing the luminous sample is placed in the receptacle R at the top of the tube T. The lens L forms an image of the preparation on the photometer cube below. The filter is shown at F. With a single filter in the arrangement shown, brightness of from 2 to 75 μL can be measured which is a greater range than is

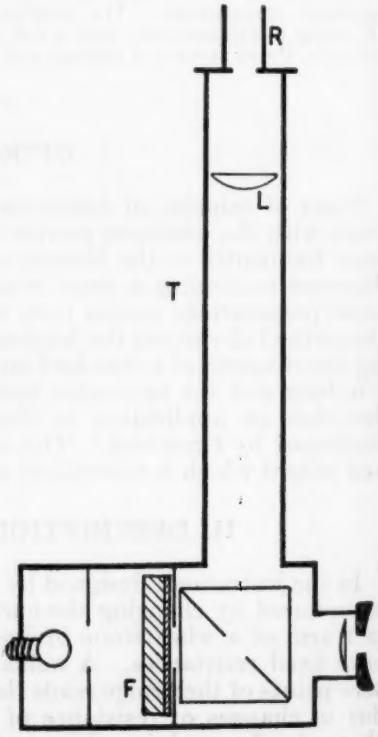

FIGURE 2.—*Diagram of arrangement of optical parts of brightness meter.*

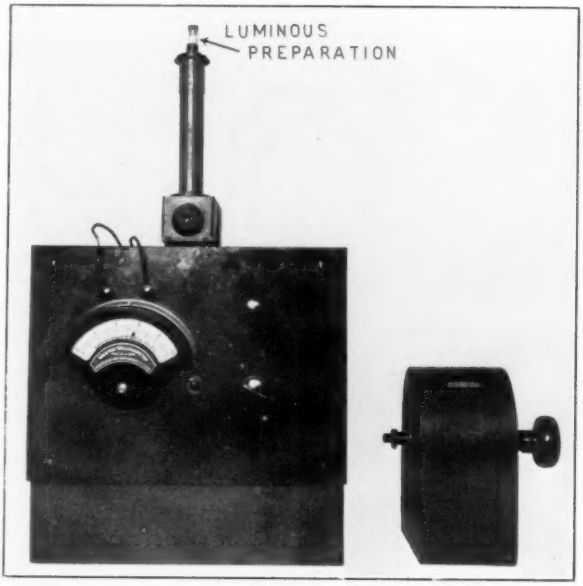

FIGURE 3.—*Photograph of complete instrument with calibration scale.*

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ordinarily met with in luminous samples, where the average brightness is about 20 μL. For calibration, a standard lamp and calibrated color filter were used to obtain settings of the milliammeter for various brightnesses. A curve was drawn and values for every half division of the milliammeter were read from the curve. These values were typed on a paper ribbon opposite the corresponding milliammeter readings so that the latter could be instantly converted into μL with sufficient accuracy. The completed instrument (left) and arrangement for converting readings into μL (right) are shown in the photograph, figure 3.

It is to be noted that the lamp is always burned well below normal voltage which greatly prolongs its life. This is important in that a renewal of the lamp requires a calibration. Another convenient feature of the arrangement is that the short circuit switch for the milliammeter, used by Crawford, is not necessary. This is because the flashlight bulb is of a vacuum type with a filament of small heat capacity; consequently when the voltage is applied the resistance of the lamp rises so quickly from its cold value that no damage is done to the meter.

The writer wishes to acknowledge the help of Miss C. L. Torrey in calibrating the meter and of B. W. Brown in its construction.

WASHINGTON, June 11, 1934.

U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP703

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August 1934

REFRACTIVE INDEX AND DISPERSION OF NORMAL AND HEAVY WATER

By L. W. Tilton and J. K. Taylor

ABSTRACT

Certain provisional values of the refractive index of normal water are given to accompany similar values determined at 25 C by the minimum-deviation method for a sample of heavy water (sp gr = 1.001376 at 25 C) using several wave lengths of the visible spectrum. According to the linear or additive relation for simple mixtures, which was found adequate in Luten's investigation, the differences in index between H_2O and H^2_2O are calculated and compared with previously published values.

According to a recent report by Luten[1] the refractive index for mixtures of normal and heavy water may be correctly computed from the mol fractions according to the linear or additive relation for simple mixtures, at least to three significant figures in $(n_1 - n)$ where n_1 and n represent the indices of normal water and of a mixture, respectively. Proceeding in this manner Luten finds good agreement between his sodium *D*-line index for pure H^2_2O and a result which he extrapolates from data for $\lambda = 5{,}876$A published by Washburn, Smith, and Frandsen[2] of this Bureau, for a sample of water having a specific gravity of 1.001376 at 25 C. Consequently it is now of interest to publish certain additional index data which at that time (February 1933) were observed for the same sample but not hitherto carefully reduced because sufficiently precise comparison data on normal water were not readily available.

These measurements were made at 25.00 C by the classical method of minimum deviation, using a water-jacketed hollow prism of 72° refracting angle and 10-ml capacity which was mounted in a stirred air bath on the spectrometer table. Temperatures were constant within ±0.01° C during these measurements and were read to thousandths by use of a platinum resistance thermometer with its sensitive element immersed in the sample. Comparatively few observations were made but otherwise all precautions appropriate for precise index determinations[3] were taken, just as is done in the absolute measurements on normal distilled water that are in progress in this refractometric laboratory, and all results refer to dry air of 760 mm pressure at the same temperature as that of the sample. Certain of these (provisional) values for the refractive index of normal water are given here (columns 2 and 3 of table 1) because the diversity among such published values precludes their satisfactory use for comparison with measured indices of heavy water.

[1] Daniel B. Luten, Jr., Phys. Rev., 45, 161–165(1934).
[2] Edward W. Washburn, Edgar R. Smith, and Mikkel Frandsen, J. Chem. Phys. 1, 288(1933); BS J.Research 11, 453–462(1933); RP601.
[3] Many requisites for precision and accuracy in minimum-deviation measurements have previously been discussed. See L.W. Tilton, BS J.Research 2, 909–930(1929)RP64; 6, 59–76(1931)RP262; 11, 25–57(1933) RP575.

TABLE 1.—*Refractive index of water*

(n_1 for H_2O, n_2 for H^2_2O, and n for mixture)

λ in angstroms	Pure H_2O referred to dry air at t C and p=760 mm Hg		$(n_1-n)\times10^7$ t=25 C		$(n_1-n_2)\times10^5$					
					t=25 C		t=20 C			
	n_1 at t=25 C	$(n^{20}_1-n^{25}_1)\times10^6$	Observed	Adjusted	Tilton and Taylor (J. K.)	Luten	Tilton and Taylor (J. K.)	Luten	Selwood and Frost corrected by Luten	Taylor (H. S.) and Selwood
					(If sp gr H^2_2O at 25 C=1.1056)					
7065.2	1.329545	475	539	531	403	.....	413	.....	.....	.....
6678.1	1.330398	478	547	546	415	.....	425	.....	.....	.....
6562.8	1.330672	479	530	551	418	.....	429	435	429	.....
5892.6	1.332502	485	586	578	439	445	450	456	473	.....
5875.6	1.332555	485	590	579	440	.....	451	.....	.....	.....
5800	.....	.....	.....	582	442	449	453	.....	.....	.....
5769.6	1.332894	486	.....	583	443	.....	454	.....	.....	.....
5460.7	1.333977	489	.....	596	452	461	463	473	.....	.....
5015.7	1.335860	493	617	614	466	.....	477	.....	.....	.....
4861.3	1.336628	495	608	620	471	.....	482	491	.....	.....
4713.1	1.337435	496	.....	626	475	.....	486	.....	.....	.....
4471.5	1.338924	499	652	636	483	.....	495	.....	.....	.....
4358.3	1.339709	500	620	641	486	.....	498	516	.....	.....
4046.6	1.342238	504	662	654	496	.....	508	.....	.....	.....
					(If sp gr H^2_2O at 25 C=1.1079)					
6562.8	.....	.....	.....	.....	427	.....	438	444	438	.....
5892.6	.....	.....	.....	.....	448	455	459	466	483	462
5800	.....	.....	.....	.....	451	459	462	.....	.....	.....
5460.7	.....	.....	.....	.....	462	471	473	483	.....	.....
4861.3	.....	.....	.....	.....	481	.....	492	502	.....	.....
4358.3	.....	.....	.....	.....	497	.....	509	527	.....	.....

Referring to table 1, the observed values of $(n_1-n)\times10^7$ for the Washburn, Smith, and Frandsen mixture were used in determining, by the method of least squares, constants in the equation

$$(n_1-n)\times10^7=818.2-407.0\lambda$$

which (with λ in microns) yields the corresponding adjusted values as tabulated for various wave lengths. Values of $(n_1-n_2)_{25}\times10^5$, n_2 being the index for H^2_2O, were then computed from $(n_1-n)\times10^7$ by the additive relation for mixtures after using Luten's nonlinear relation between specific gravity and composition to determine a value $N_2=0.01318$ for the mol fraction of H^2_2O in this particular sample of heavy water. Luten's temperature coefficients of index of H^2_2O were used in deriving $(n_1-n_2)_{20}\times10^5$. Table 1 also includes values of $(n_1-n_2)\times10^5$ as reported by Luten and by other observers.[4]

Since Taylor and Selwood[5] have announced a value of 1.1079, instead of 1.1056 as previously used, for the specific gravity of H^2_2O at 25 C and also a refractive index determined for such water, all of these previously considered results have been revised and are recompared in the lower portion of table 1. The new value for the mol fraction of the Washburn, Smith, and Frandsen sample of heavy water becomes 0.01290.

[4] P. W. Selwood and A. A. Frost, J. Am. Chem. Soc., **55**, 4335(1933).
[5] Hugh S. Taylor and P. W. Selwood, J. Am. Chem. Soc., **56**, 998(1934).

In general, the various values of $(n_1 - n_2)$ show good agreement. It should be noticed that the extrapolation from the sample of specific gravity 1.001376 would propagate an error of 1 in the sixth decimal place of n or n_1 to 8 in the fifth decimal of n_2. As compared with Luten's results, the slightly higher index and higher dispersion for the sample measured in this laboratory may, therefore, be the result of very slight systematic errors in measurement but it should be remembered, also, that Washburn, Smith, and Frandsen gave some results which indicate that some O^{18} should be present in this sample. According to the provisional data given by Lewis and Luten,[6] an excess atom fraction of 0.001 for O^{18} would account for the difference in these values of $(n_1 - n_2)$ as tabulated for wave length 5800 A.

TABLE 2.—*Dispersion of water for specified intervals of wave length*

$\triangle n_1 \times 10^5$ for normal water

Observer	Temperature	4047 to 4358 A	4358 to 4861 A	4861 to 5461 A	5461 to 5893 A	5893 to 6563 A	6563 to 7065 A	4358 to 6563 A
	° C							
Tilton and Taylor (J. K.)	25	252.8	308.1	265.1	147.5	183.1	112.7	903.8
Do	20	253.2	308.7	265.6	147.9	183.6	113.2	905.8

$\triangle n_2 \times 10^5$ for pure H^2_2O

Tilton and Taylor (J. K.)	25	243	292	247	134	162	97	835
Luten	20		288	245	132	161		826
Selwood and Frost	20					160		

The apparent lower dispersion that might be inferred for n_2 from the Selwood and Frost values of $(n_1 - n_2)$ is a result of the unusually high dispersion of the values which they tabulate for "ordinary water", namely, $(n_D - n_C) \times 10^5 = 199$ at 20 C. Their tabulated indices for all three solutions of heavy water yield reasonable values of dispersion and, as shown in table 2, their computed results for H^2_2O yield a difference, $n_D - n_C$, that is in good agreement with Luten's value and with the data of this paper.

WASHINGTON, May 28, 1934.

[6] G. N. Lewis and D. B. Luten, Jr., J.Am. Chem. Soc., 55, 5062(1933).

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EQUIPMENT FOR MEASURING THE REFLECTIVE AND TRANSMISSIVE PROPERTIES OF DIFFUSING MEDIA

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ABSTRACT

The construction and operation of equipment is described for studies of the diffusion and absorption of light by materials such as textiles, papers, paints, enamels, and other diffusing media for which measurements of color, gloss, transparency or optical density, hiding and tinting powers, or similar properties, are required. Means are provided for the precise control of the directional and spectral distributions of light incident on the sample and for measurement of the corresponding distributions of diffused light.

The equipment includes two separate illumination units, one for completely diffused illumination of the sample and the other for unidirectional illumination at any desired angle of incidence. Light reflected or transmitted by the sample under either type of illumination is measured for any desired direction of observation by visual photometric or spectrophotometric methods.

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I. INTRODUCTION

Many problems in diverse fields of science and industry call for studies of the diffusion[1] and absorption of light by optically nonhomogeneous materials such as textiles, papers, paints, ceramic bodies, illumination glassware, photographic plates or films, and liquid suspensions of finely divided particles. The distribution of the diffused light, with respect to direction and wave length, is determined by the composition, structure, and form of the diffusing medium and by the directional and spectral distribution of the in-

[1] The word diffusion is employed herein to cover a multitude of refractions, reflections, diffractions, and Rayleigh scattering, taking place at the surfaces or within the body of the diffusing medium, by virtue of which there is a general directional redistribution of the incident light.

cident light. In some problems the immediate objective is the establishment of definite relations between elements of composition or structure and the observed distributions of light. In other cases the nature of the medium itself is a secondary consideration, and we are concerned chiefly with the numerical description of properties such as the color, gloss, and surface texture of fabrics, papers, and painted or enameled surfaces, the hiding and tinting powers of paints and enamels, the transparency and optical density of printing papers, tracing papers, or photographic films, and other characteristics of similar nature for which optical methods of specification are required.

In an analysis of the color of a given material we deal chiefly with the spectral distribution of light incident on the sample and with the change in this distribution brought about by the sample (absorptive properties). The physical factors determining the appearance of gloss, on the other hand, are to be found chiefly in the directional distributions of the incident and diffused light (diffusive properties). It is common experience, however, that the color of a material often varies markedly with the directional distribution of the incident light or with the particular direction chosen for the observations. Likewise, in the derivation of any adequate specification for gloss we cannot ignore the effect of the light distributions with respect to wave length. Gloss is dependent to a large degree on the absorptive properties of the material. Hence, diffusion and absorption, involving directions and wave lengths, are inextricably interrelated in the problems of colorimetry and glossimetry.

In present colorimetric practice there is not universal agreement in regard to directional conditions, or sets of such conditions, which should be adopted for various purposes of colorimetry.[2] Little quantitative information is available on the magnitude of color differences to be encountered under varying directional conditions of illumination and observation. The problem becomes most acute perhaps in the colorimetry of textile materials, because of the great range of colors, variable surface texture, and body structure presented by this class of materials.

In the evaluation of the hiding and tinting powers of paints and enamels we deal with materials for which certain elements of structure may be known, such as the size distribution, shape, or concentration of the pigment particles, along with the compositions and the refractive and absorptive properties of individual particles and the embedding medium. Under suitably prescribed conditions of illumination and observation the problem may consist (1) in the development of numerical expressions for hiding and tinting powers, and (2) in the relation of these properties to certain characteristic structural parameters, so that the performance of the material may be better understood and its behavior predicted as the parameters are changed. Such problems are fundamental in the paint and enamel industries.

The choice of the conditions of illumination and observation for photographic density measurements has long been the subject of controversy in quantitative photographic testing and research.

[2] See table 1 for the single directional condition adopted byi nternational agreement.

Density values depend on the directional and spectral distributions of light employed in the measurements. Different densities may be defined and measured and are useful for various purposes.

Other illustrative problems include the measurement of transparency and printing opacity of papers, multiple reflection methods for precision colorimetry of nearly white materials, specifications of surface finish or smoothness as indicated by reflective or polarizing properties, and the development and specification of material standards for use in colorimetry and photometry.

It is the purpose of this paper to describe equipment which has been assembled for investigations such as indicated above. Means are provided for controlling the directional and spectral distributions of light projected on the sample and for measuring the corresponding distributions of diffused light. Various diffusive and absorptive properties derived from such measurements provide the physical basis for a rational treatment of the suggested problems, but specific applications of the equipment are not included in the scope of the present paper.

II. FIXED CONDITIONS FOR THE MEASUREMENTS

In the most general condition of illumination on the sample the distribution of intensity and polarization in the incident light may vary continuously or discontinuously in any complex manner with direction of incidence and with wave length. Some investigations may call for a particular form of sample or for some special condition of illumination. Most purposes will be adequately served, however, if the form of the sample and the available types of illumination are limited to a few fixed, or standard, reproducible conditions under which the diffusive and absorptive properties are defined and measured.

The following conditions are established to a close approximation by the construction of the apparatus herein described:

(1) *The sample* is in the form of a slab of uniform thickness, composition, and structure, throughout its entire lateral extent. This extent is such, relative to the thickness and point of observation (S, fig. 1), that edge effects are always negligible.

(2) *The conditions of illumination are constant* over the entire extent of the sample, so that various coefficients of reflection and transmission may all be referred to unit areas of the reflecting and transmitting surfaces.

Each coefficient is a ratio of light reflected or transmitted per unit area to light incident per unit area, and includes in its definition specific directional and spectral conditions of illumination and observation. The various coefficients are conveniently classified into groups, each group corresponding respectively to some one definitely specified condition of illumination[3] and including various conditions of observation. In table 1 the conditions of illumination are divided into two main groups, corresponding, respectively, to restrictions imposed on the directional and spectral distributions of incident light.

[3] Some coefficients of reflection, their interrelation and measurement, have been defined and discussed by the author in B.S. J.Research 1, 29(1928); RP3. Further definitions of this kind may be taken up as needed in future work.

(3) *Unidirectional illumination.*—The condition of illumination is defined as unidirectional when the incident light is distributed over a small range of directions, so small that any further reduction in range would have no appreciable effect on the measurements to be made. In the present equipment the source is such that throughout the lateral extent of the unidirectional beam the polarization is nil and the intensity and its spectral distribution are independent of the direction of incidence on the sample.

(4) *Completely diffused illumination.*—The illumination is completely diffused when it is obtained by the superposition of unidirectional incident beams, each of which fulfils conditions (2) and (3) as specified above, and all together cover continuously the complete range of incidence directions represented by the solid angle of 2π with vertex at any point on the illuminated surface.

The diffusive and absorptive properties for any type of multidirectional or partially diffused illumination between the two extreme

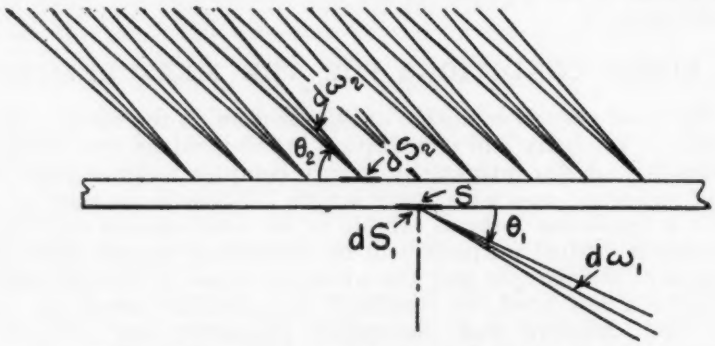

FIGURE 1.—*Diagram of unidirectional incident beam.*

types here defined may always be derived by addition of effects as observed separately for various modes of unidirectional illumination. No particular type of partially diffused illumination appears at present to be of sufficient practical interest to be classed as a standard condition.

The unidirectional and completely diffused types of illumination are of particular interest as standard conditions because of the reciprocal relations which have been shown to exist between certain groups of reflection and transmission coefficients. These relations have been discussed at length in other publications[4] and are of considerable importance in the applications of the equipment.

(5) *Homogeneous illumination.*—In the above specification of directional conditions the relative spectral distribution of incident light remained arbitrary. When the spectral distribution of incident light covers a small range of wave lengths, so small that further reduction in range would have no appreciable effect on the measurements, then the illumination is defined as homogeneous with respect to wave length.

[4] Meslin, Ann. de Phys. [9] 1, 297 (1914). McNicholas, BS J.Research, 1, 29 (1928) RP3; Boutaric, Rev. d'Opt., 10, 485,(1931).

The reciprocal relations have been defined between coefficients of reflection only. Corresponding relations apply equally well, however, between the corresponding coefficients of transmission.

(6) *Composite illumination*, heterogeneous in wave length. In analogy with the condition of partially diffused illumination the diffusive and absorptive properties for any special type of composite illumination might be derived by addition of effects observed separately for the different homogeneous components. The extensive observations and computations involved are often avoided, however, by making observations directly under the given spectral distribution of incident light. Standard conditions of composite illumination for colorimetric purposes are indicated in table 1.

TABLE 1.—*Conditions of illumination commonly employed in reflectometry and transmissometry*

Directional conditions		Spectral conditions	
Type	Special cases	Type	Special cases
Unidirectional	Incidence at 0° Incidence at 45° [1]	Homogeneous with respect to wave length.	Any wave length in visible spectrum.
Partially diffused	No special case generally employed or of particular interest.	Composite, or heterogeneous with respect to wave length.	Illuminant A.[1] Illuminant B.[1] Illuminant C.[1]
Completely diffused	Frequently used in photometry and spectrophotometry.	Equal energy at all wave lengths.	Not easily realized in practice.

[1] Adopted as standard conditions in colorimetry by international agreement. Proceedings of the 8th session, Comm. Int. l'Eclairage, Cambridge, p. 19 (1931). Unidirectional illumination at 45° incidence adopted for reflectance measurements only. Illuminants A, B, and C approximate closely to the gas-filled lamp, average noon sunlight, and average daylight, respectively.

III. DESCRIPTION OF APPARATUS

A plan of the assembled equipment is shown in figure 2. Many details of the construction and operation of different units of the assembly, not included in the text, are given in the legends to the various figures.

The two fixed directional conditions of illumination, as defined above, are respectively realized to a sufficient approximation by the construction of two separate illumination units, one for unidirectional and the other for completely diffused illumination of the sample. These units contain incandescent-filament lamps emitting light covering a continuous extension in wave length over the entire range (visible spectrum) required for the intended applications of the equipment. For a given directional condition of illumination the desired control of the relative spectral distribution of incident light is effected by use of selective light filters of various kinds, including, for homogeneous illumination, the highly selective dispersion system of a spectrometer. Excluding the case of strongly fluorescent diffusing media, in which there is an appreciable transformation of light from a given wave length to other wave lengths, it is well known that the overall intensity gradient along any ray path from the source through the sample to the light-sensitive receiver is independent of the sequence in position along that path of selective light filters of any kind. Consequently, the desired control of the spectral distribution of incident light is accomplished effectively and most conveniently in the

present equipment by placing the selective light filter between the sample and the receiver, instead of attempting a direct control of the illumination itself. This is the usual procedure in photometry and spectrophotometry when a unidirectional observing beam is employed.[5]

The complete assembly of apparatus consists essentially of the two illumination units with sample holders, a ventilation system, and the photometric equipment, which contains the selective light filters for effective control of the spectral conditions of illumination on the sample. The photometric equipment is stationary and the sample is always observed in a fixed horizontal direction. To provide for variations in the directions of illumination or observation the observed surface of the sample and the positions of the light sources may be oriented differently with respect to the fixed direction of observation. A part of the photometric equipment (comparator and sectored-disk

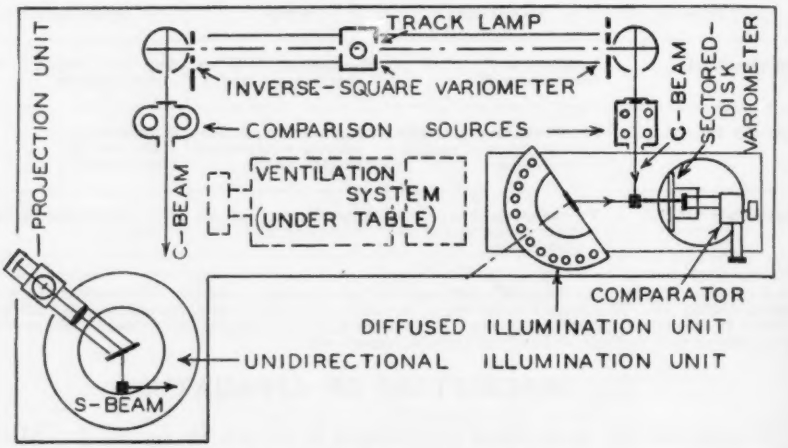

FIGURE 2.—*Plan of assembled equipment.*

variometer, fig. 8) is mounted on a single detachable base-plate and may be transferred readily from one illumination unit to the other.

The intensity and polarization of an unidirectional homogeneous or composite beam of light, as received from the sample under either type of illumination, is measured by ordinary visual photometric procedure, using either the equality-of-brightness of minimum-flicker methods of photometry.

1. UNIDIRECTIONAL ILLUMINATION UNIT

The construction of the unidirectional illumination unit is shown in figures 3 and 4. In each figure the source and sample are in proper position for photometric measurements on the sample by transmitted light.

The source (1) is a 1,000-watt projection lamp with its coiled filaments centered on the common axis, and lying in the common principal focal plane, of a plano-convex lens (11) and concave mirror (13),

[5] Equipment in which the selective light filter is placed between the source and sample is described, for certain limited applications, by Gibson (J. Opt. Soc. Am. and Rev. Sci. Instr., **18**, 166 (1929); **21**, 144 (1931).) This method is also incorporated in the photoelectric spectro photometer of Hardy (J. Opt. Soc. Am. **24**, 162 (1934).

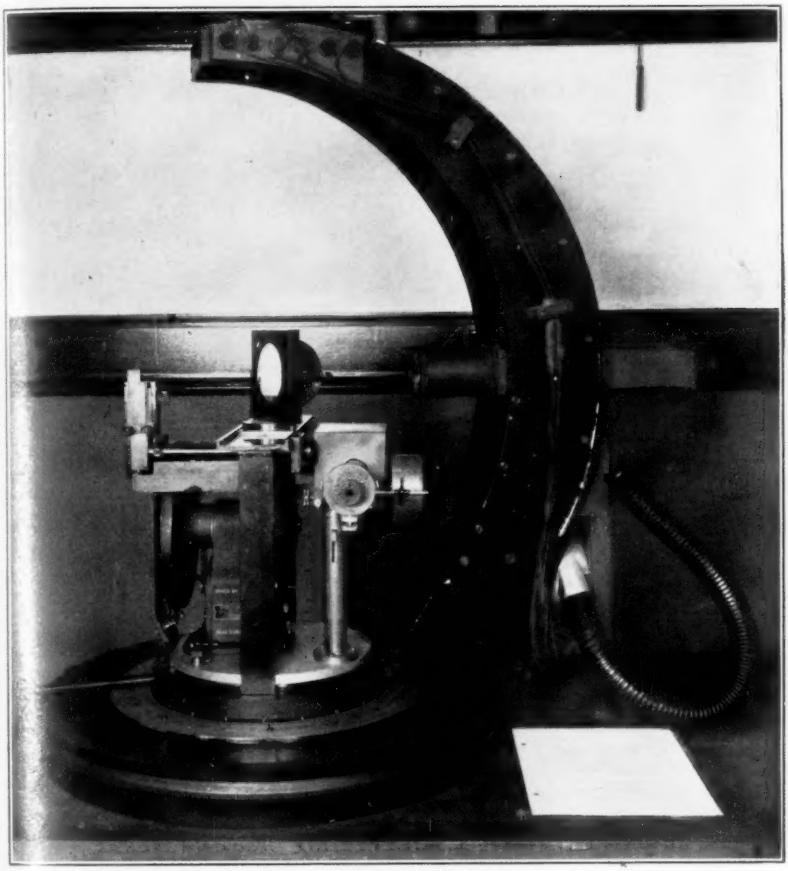

FIGURE 3.—*Apparatus for reflection and transmission measurements with unidirectional illumination of the sample.*

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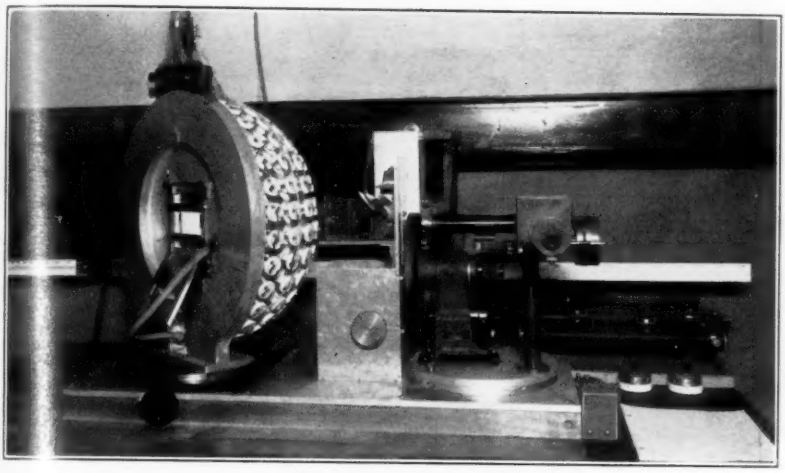

FIGURE 5.—*Apparatus for reflection and transmission measurements with completely diffused illumination of the sample.*

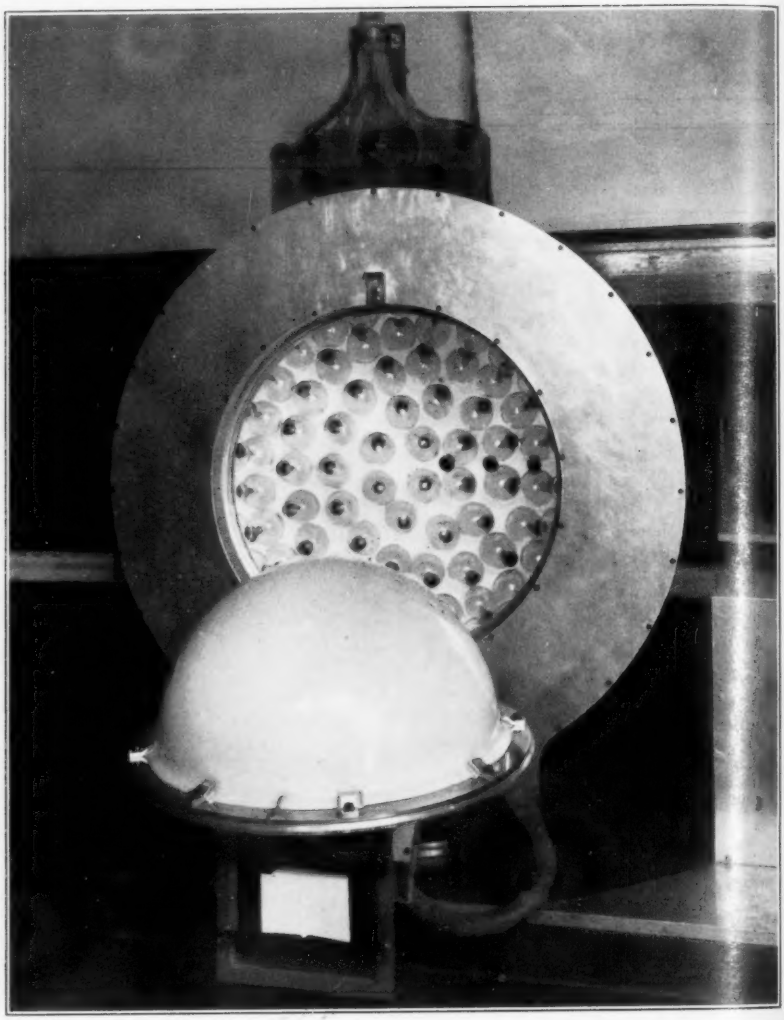

FIGURE 6.—*Hemisphere source for completely diffused illumination, showing opened door carrying milk-glass hemisphere and arrangement of lamps on white-lined steel hemisphere.*

so that an intense undirectional beam is thus defined and projected toward the center of the sample. A small blower (9) delivers a strong blast of air directly against the base of the lamp, a provision for cooling which is necessary in order to operate this lamp continuously in the small blackened box (3). The lamp box and blower, together with lens and mirror supports, are all mounted as a unit on a rigid frame (16). This unit is in turn supported by the large arc-shaped frame (19) and is free to slide on the vertical circular track (20), which is centered at the center of the sample. The entire projection unit may be moved and clamped at any desired position on the circular track, so that the undirectional beam is directed onto the sample at any desired angle from the horizontal to the vertical.

The arc-shaped support for this projection unit is mounted on a heavy circular iron base (24) so that the source may be rotated through 360° about a vertical axis passing through the centers of the base and sample.

The mounting of the sample permits of three degrees of rotational freedom. It may be rotated through 360° about a vertical axis and through 180° about a horizontal axis. Both axes pass through the center of the sample with the horizontal axis lying in the plane of the illuminated surface. In addition, the sample may be rotated in its own plane about an axis through its center and normal to its surface. Circular scales indicate the amounts of these rotations.

In the figures and the text the fixed horizontal unidirectional beam of light, proceeding from the sample to the photometric system, is always designated as the S-beam. The complete sample holder (42) slides between guides on a horizontal table (40), the direction of motion being perpendicular to the direction of observation (direction of S-beam). A transmission or reflectance standard (41) is mounted on the same table, so that the sample may be moved quickly and conveniently from the path of the incident beam and the comparison standard substituted in its place. The standard is held in a fixed position on its holder. Its reflective or transmissive properties are either known for various positions of the source, or the source may always be brought to some specified position, such as 0° incidence, when the comparison standard is being observed.

The central raised portion of the circular base plate (24) carries a part of the photometric equipment. This equipment is described in section III along with other parts of the photometric system shown inclosed in box (46).

The three degrees of freedom of the sample, with the two degrees of freedom of the source, permit combinations of all desired directions of incidence and observation for any sample. In this connection the Helmholtz reciprocity law [6] may be applied to great advantage, because every measurement made with a particular combination of directions of incidence and observation has its reciprocal interpretation as a measurement for reversed directions of incidence and observation.

With the 1,000-watt lamp operating at normal voltage, and using a collimating lens (11) of 20 cm focus, the brightness of a magnesium carbonate block for 0° incidence and 45° observation is approximately 5.8 lamberts.

In the measurement of the directional distribution of light over a range of directions through which the intensity gradient is very steep

[6] See footnote 4.

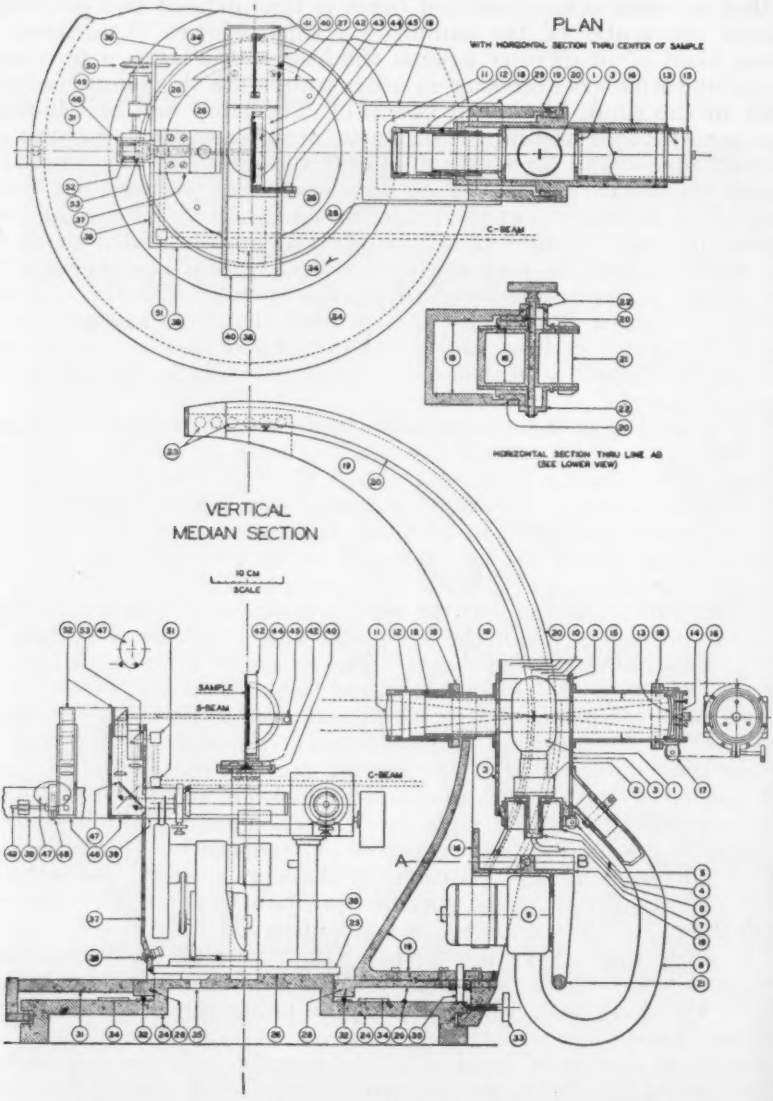

FIGURE 4.—*Construction of unidirectional illumination unit.*

1. Gas-filled tungsten-filament projection lamp, 110 volts, 1,000 watts.* *2.* Mogul base lamp receptacle; upper part of porcelain body cut away, thus exposing metal parts for better cooling. *3.* Blackened lamp box. *4, 5, 6.* Vertical, lateral, and rotational adjustments of lamp. *7.* Current leads through bakelite bushing. *8, 9.* Flexible metal tube and air blower for forced ventilation of lamp box. *10.* Removable top of lamp box, obstructing passage of light but permitting free egress of air. *11.* Plano-convex lens, focal length 20 cm, diameter 6 cm. Lens of 30 cm focus also provided. *12.* Lens support held rigidly to frame (16). *13.* Concave silvered-glass mirror, 20 cm focal length, centered on axis of lens at focal distance from plane of lamp filaments. *14.* Support and adjustments for mirror holder. Mirror forms image of lamp filaments in space between coils. Intensity of collimated beam thereby increased 70 percent. *15.* Mirror support mounted rigidly on lamp box. *16, 17.* Brass frame supporting lamp box, lens, and mirror tubes, and ventilating blower. Loosening clamp (17) permits lamp box with mirror tube to be moved on frame parallel to axis of lens, thus adjusting plane of lamp filaments in focal plane of different lenses. Lenses from 20 to 30 cm focal length may be accommodated. *18.* Telescoping tubes. *19.* Aluminum frame supporting two arc-shaped brass guides (20), which form a vertical circular track having sample at center. *20.* The brass frame (16), supporting entire projection unit, slides freely on circular track (20), keeping axis of lens pointing to center of sample. *21, 22.* Handle and clamping device for projection unit. See section view through frame (19) along line AB. Circular scale (not shown) engraved on one arm of frame (19) gives position of source on circular track. *23.* Terminals for current leads. *24.* Cast-iron cir-

(reflection from glossy sample near the angle of specular reflection) it may be found that the incident beam no longer fulfills the condition for unidirectional illumination as prescribed in section II, condition (3). If so, the directional extent of the incident beam, and hence the resulting error in the intensity measurement, may be reduced by the use of a projecting lens of longer focus. Provision for such adjustment has been made, as explained in the legend to figure 4, items 16, 17, and 19. The directional extent of the observing beam is determined by the construction of the comparator (sec. III, 3, (a)) and is considerably less than that of the incident beam, so that the required condition is in this case readily fulfilled. These possible errors in the measurement of directional distributions are analogous to the slit-width errors well known in ordinary spectrophotometry, which arise from the use of a measuring beam containing too large an extension in wave length.

2. DIFFUSED ILLUMINATION UNIT

The construction of the source for completely diffused illumination is shown in figures 5, 6, and 7, with a detailed description of various parts in the legend to figure 7.

The illuminated plane surface of the sample forms a part of the base of a milk-glass hemisphere (19), the inner concave surface of which, as viewed from the position of the sample, is of uniform brightness over all its parts. This fully extended source of uniform brightness is obtained by direct illumination of the outer convex surface of the translucent hemisphere by means of a concentric hemispherical arrangement of one hundred and four 27 cp lamps (21). These lamps are uniformly distributed over the inner concave surface of a larger concentric steel hemisphere (20), with the axis of each lamp pointing toward the common center of the hemispheres. The lamp bases project through circular holes in the steel hemisphere and each lamp is supported with its receptacle on the outer surface. Approximately 7 percent of the total area of the inner surface of the steel hemisphere is taken up by the openings provided for the lamp bases; the remaining surface is covered with a double coating of white porcelain enamel (baked) over which a film of magnesium oxide is deposited. The white diffusely reflecting surface thus obtained considerably increases

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cular base, 58 cm in diameter. Central raised part carries base plate (25). *25.* Base plate carrying parts of photometric equipment which are transferable from one illumination unit to the other. See also figures 3, 5, and 8. This equipment is removed in upper plan view. *26.* Flat upper surface of raised portion of base (24). *27.* Guiding edge for base plate (25), permitting accurate alignment of photometric equipment on surface (26). See corresponding edge of base plate (25) in figure 8. *28.* Circular guide ring with bearings as shown, and with two projecting arms, (29) and (31). Rotates about vertical axis through center of base. *29, 30.* Arm-plate and ball-bearing roller supporting frame. (19). *31, 32.* Balancing arm and ball-bearing race. *33, 34.* Clamp for horizontal motion and circular scale. *35, 36.* Hole in base and binding posts for detachable electrical connections to sectored-disk motor. *37, 38, 39.* Supports for box (46), table (40), and other parts. *40.* Table for support of sample and standard. Base plates of sample and standard holders slide between guides on edges of table top, so that sample and standard may be alternately brought into proper position for illumination and observation. *41.* Holder for reflection or transmission standard. Position stationary on holder. *42.* Holder for sample. Sample may be rotated about horizontal and vertical axes through its center and about axis perpendicular to its surface. *43.* Horizontal circular scale. *44.* Vertical semicircular scale. *45.* Clamp and index. *46.* Box containing prisms and lenses for directing light beams to the comparator. *47.* Flicker disk, 4 cm in diameter, similar in construction to disk in figure 7, item (11). The three views show position of disk relative to light beams. *48.* Disk mounted on shaft outside of box (46) and connected by bevel gear to shaft (49). Adjustment for disk in beams is provided. *49, 50.* Shaft and pulley transmits motion to flicker disk. Pulley connected by belt to motor located under table. Other pulleys (not shown) guide belt down side of (38) and through raised part of base (24), between guiding edge (27) and rotating ring (28). Hence, belt line does not interfere with the insertion or removal of the photometric equipment mounted on base (25), or with the free rotation of arm (19). *51.* Prisms guiding C-beam to comparator. *52, 53.* These prisms are mounted so that they may be moved vertically from outside of the box until (53) intercepts the S-beam and (52) intercepts the C-beam. This operation interchanges the S- and C-beams through the sectored-disk variometer, thus greatly extending the range of this instrument.

the magnitude and uniformity of the illumination over the translucent milk-glass hemisphere. The equatorial plane of the two concentric hemispheres is a nickel-plate mirror surface (30) on a thin brass plate.

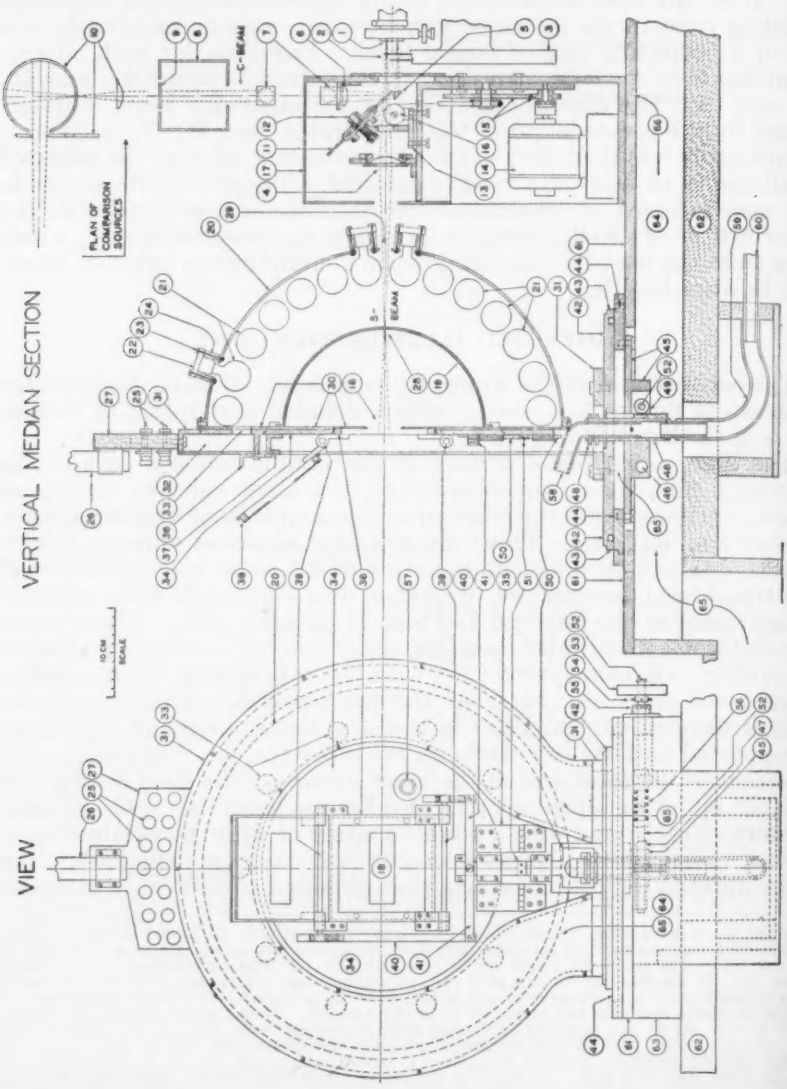

FIGURE 7.—*Construction of diffused illumination unit and parts of photometric equipment.* See p. 221.

A rectangular aperture (18), centered on this base, is covered by the sample or a comparison standard. Apertures of different size [7] may be used.

[7] The area of the illuminated portion of the sample is important. It should be large enough so that edge effects are always negligible (condition 1, sec. II), and small enough so that the reflectance of the sample has no appreciable influence on the average reflectance of the hemisphere and its base. The edge effect is the reduction in the observed brightness of the sample which is due to the uncompensated loss of light through the edges. It is only significant for thick samples of a material such as milk-glass. The average reflectance of the walls of the hemispherical inclosure determines that part of the total illumination of the sample (hence its brightness) which is due to multiple reflections within the inclosure. For a given aperture this reflectance effect is readily calculated and eliminated by a correction formula; its magnitude has been calculated for certain cases by Hardy and Pineo J. Opt. Soc. Am. (**31,** 502(1931).

The hemisphere lamps are arranged on seven equally spaced parallels of latitude and so connected electrically that the current in each ring of lamps is independently adjustable. Some small adjustment of these currents is required to obtain the desired uniformity of brightness over the entire inner surface of the milk-glass hemisphere. Measurements of this brightness distribution, as seen from the sample, showed a residual maximum variation of about 3 percent, but the variation was less than 2 percent over the larger part of the hemisphere.

The illumination on the sample from this hemisphere source fulfills condition (4) of section II to a sufficient approximation for all diffusing media. With the lamps operating at normal voltage the brightness of a magnesium carbonate sample observed normal to its surface is approximately 6 lamberts.

The white-lined reflecting hemisphere supporting the lamps is mounted on the aluminum casting (31), with the base of the hemisphere in a vertical plane. The milk-glass hemisphere is mounted on a

1. Collimator (or entrant) slit of comparator. *2.* Sectored disks in light beams. *3.* Sectored-disk variometer. *4.* Lens focusing collimator slit in plane of circular aperture (28). *5.* Small total-reflection prism causing C-beam to intersect S-beam at right angles. *6.* Lens controlling spread of C-beam. *7.* Prism giving C-beam again a horizontal direction, so that light may be taken from comparison lamp box (8) or from inverse-square variometer (10). *8, 9.* Comparison lamp box with removable portion of wall (9). *10.* Parts of inverse-square variometer. See figures 2 and 10. *11.* Flicker disk, 10 cm in diameter. Steel plate with two open 90° sectors. Surfaces of plate first polished and then electroplated with chromium. *12.* Axle and pulley for rotation of disk. *13.* Support for flicker disk, with adjusting screws for proper orientation of disk in light beams. *14, 15, 16.* Motor, reducing gear, and pulleys for belt drive of flicker disk. *17.* Removable cover. *18.* Aperture covered by sample (or standard). The illuminated surface of sample lies 1 mm back from mirror surface. *19.* Milk-glass hemisphere such as used for ceiling bowls in lighting installations. Diameter 23 cm; average thickness 2.5 mm; inner concave surface fine-ground with sand blast. *20.* Steel hemisphere, spun from no. 18 gage sheet enameling stock. Diameter 40 cm; inner concave surface covered with two coats of white porcelain enamel (baked), and then "smoked" with magnesium oxide from burning magnesium shavings. *21.* Gas-filled tungsten-filament lamps, 9-volt 27 cp (approximately 18 watts). Tipless spherical bulb 35 mm in diameter; candelabra screw base. First ring about pole contains 4 lamps. Other rings contain 10, 17, 23, 28, 30, and 31 lamps, respectively. Lamps connected in series-parallel arrangement and operated on 110-volt supply line. The 14 lamps in the first two rings from the pole form one of the series. Other rings are each divided into two separate series with a variable length of resistance wire in each circuit for current adjustment. *22, 23, 24.* Porcelain lamp receptacle (22) is supported on hemisphere by bolts (23) passing through hemisphere and brass tubes (24). *25, 26, 27.* Binding posts, wires, and hard-rubber supports for electrical connections to lamps. *28.* Aperture 6 mm in diameter at pole of milk-glass hemisphere. Six similar apertures are located in the horizontal meridian plane at different angular distances from the polar axis. See text. *29.* Aperture 15 mm in diameter at pole of steel hemisphere. Six similar apertures correspond in angular position to apertures (28). *30.* Mirror base; nickel plating on brass. *31, 32, 33.* Aluminum casting (31) forms support for hemispheres and other parts. Two flanges, with a cover plate, on the outer part of the casting forms the horse shoe-shaped compartment (32), from which air for ventilation purposes passes through holes (33) and out through annular openings around the lamp bases. *34, 35.* Circular plate (34) carrying milk-glass hemisphere and other parts is mounted on hinges (35) forming door-way into outer hemispherical inclosure. *36, 37.* Latch and handle for door (34). *38.* Holders for sample and standard form square doors into the milk-glass hemisphere inclosure and are rigidly attached to shafts (39). *39.* Shafts simultaneously rotated by rack-and-pinion arrangement, thus swinging sample or standard alternately into proper position for measurements. *40.* Rectangular bars having teeth cut in upper ends. These teeth mesh with teeth in pinion wheels which are rigidly attached to shafts (39). Bars slide in shallow grooves cut in plate (34) and connect with cross bar (41). *41.* Vertical motion of cross bar operates rack-and-pinion arrangement. Shifting mechanism explained below. *42.* Circular brass plate with bearing on a rectangular brass plate (44). Circular plate may be rotated through 360° about a vertical axis passing through its center and lying in the illuminated plane surface of the sample. The circular plate is held in position by guides (not shown) bearing on outer edge of the plate and centered on the diagonal lines of the rectangular plate (44). There is thus no side thrust on tube (48). *43.* Circular scale for reading angular position of source. *44.* Rectangular brass plate carrying entire source is movable between guides in a direction perpendicular to S-beam. *45, 46, 47.* The crosspiece (45) carries part of sample shifting mechanism and a hole (46) which is threaded for the large screw (47). This screw extends outside the base of the instrument and is used to effect the horizontal motion of plate (44). *48.* Circular brass tubing bearing in crosspiece (45) and centered on vertical axis of rotation. The tube is movable in a vertical direction by rack-and-pinion arrangement (49), but does not rotate with the circular base plate (42). Two flanges on the upper part of the tube make sliding connection with the slide bar (50). *49.* Rack-and-pinion. *50.* Slide bar transmits vertical motion of tube (48) to cross bar (41), for any angular position of source. *51.* Slide bar is cut and parts connected by two headless pins, thus permitting the free opening of door (34). *52.* Shaft connecting pinion of (49) to handwheel (53). Pinion is keyed to shaft, and an extended keyway permits horizontal motion of plate (44), while shaft remains stationary. *53, 54, 55.* Handwheel (53) is keyed to shaft (52). An extended keyway permits locking of the shaft by meshing of pins (54) with teeth (55) on shaft bearing. *56.* Shaft (52) is split and connected by a heavy steel spring, permitting tension to be applied to sample shifting mechanism before locking handwheel. Sample (or standard) holder (38) is thus held firmly in position for measurement. *57.* Entrance and support for high-velocity air jet, which is directed on sample for cooling purposes. *58.* Brass tube freely rotating in tube (48) and connected by rubber tubing to air jet. *59.* Rubber tube connection permitting free motion of sample shifting mechanism. *60.* Connection to air filter. *61, 62.* Main base plate and table top. *63.* Square-section wood pieces raising base (61) from table top (62) to form compartment (64). *64.* Compartment connected to air supply for ventilation purposes at (65). *65.* Arrows show course of air between compartments (64) and (32). *66.* Air stream to comparison lamp box (8). See figure 9, right-hand diagram.

circular door (34) which may be opened for inspection or renewal of the lamps, or for adjustment of the position of the milk-glass hemisphere. Figure 6 shows the opened position of the door and the arrangement of lamps on the white hemispherical background.

In the same figure a series of seven small holes in the milk-glass hemisphere may be seen extending along one meridian from the pole to the base. There are also seven corresponding but larger holes in the outer hemisphere. When the door (34) is closed the two series of holes are centered in the horizontal meridian plane common to both hemispheres, at angular distances of 0, 12.0, 25.5, 38.5, 51.0, 63.0, and 77.0°, respectively, from the polar axis. The entire hemisphere source, with the sample, is free to rotate through 360° about a vertical axis through the center of the illuminated surface of the sample. Corresponding pairs of observation holes may thus be brought in line with the stationary S-beam to the photometer and the sample observed by reflected light at the above-given angles from the normal to its surface.

The holes at the poles of each hemisphere are shown in figure 7. The conjugate focus of the entrant slit of the comparator (sec. III, 3, (a)) is formed by lens (4) approximately in the plane of the aperture in the milk-glass hemisphere. This permits the smallest possible diameter of this aperture and properly limits the observed area of the sample. This area, for observation at 0°, is semicircular in outline and approximately equal to 0.5 sq cm.

For angles greater than 90° the sample is observed by transmitted light. Because the vertical axis of rotation lies in the illuminated surface of the sample it is evident that for thick samples the observed area of the transmitting surface will be shifted appreciably for grazing angles of observation. In order to maintain the center of the observed area fixed as the source and sample are rotated about the vertical axis, the entire source may be moved by a prescribed amount between guide bars on the main base plate (61) and in a direction which is perpendicular to the fixed direction of observation. The required movement is a known function of the thickness of the sample and the angle of observation.

Thus the brightness of the sample may be observed by transmitted or by reflected light. The sample may be rotated in its own plane so that observations may be made at any desired azimuth as well as at various angles from the normal to its surfaces. Because of the symmetry of the illumination these data suffice for a complete determination of the diffusive properties of any type of material.

In the photometric procedure generally employed (described in section IV) it is necessary to bring the sample and a standard material alternately in position for measurement, and it is desirable that this operation be performed in a manner which is rapid and convenient for the observer. Furthermore, the mechanism serving this purpose must operate equally well for any given angular position of the source. These requirements are met in a satisfactory manner by the mechanism shown in figure 7 and explained in the legend. The sample holder is itself a square door into the milk-glass hemisphere inclosure, and is rigidly attached to the lower shaft (39). A similar holder for the standard is likewise attached to the upper shaft (39). These shafts are simultaneously rotated by rack-and-pinion arrangements operated

by a hand-wheel (53), which is within easy reach of the observer. As the sample holder is swung out from the base of the hemisphere, the holder carrying the standard is simultaneously lowered into place. The holders accommodate a sample 10 cm square and of varying thickness. Cross-bars with spring clips and other special devices hold the sample and standard firmly against the openings in their respective holders.

The sample need only be exposed to the radiant heat from the source during the time required for a brightness measurement. It is then swung away from the source and replaced by the comparison standard, thus having an opportunity to cool while exposed to the outer air. An additional cooling of the sample and a ventilation of the milk-glass hemisphere inclosure is provided by a high-velocity jet of air which is directed on the sample (when in position for measurement) at an angle of approximately 50° from the normal by means of a glass nozzle tube. This tube enters the hemisphere inclosure through a brass support at (57), where it is connected by rubber tubing (shown in figure 5) to the brass tube (58). This tube is free to rotate (with the hemisphere) in the stationary tube (48), which is in turn connected through an air-filter to the air supply (sec. III, 4).

The high-velocity air jet is very effective in the cooling of the surface of the sample, but the volume of air thus delivered is not sufficient for proper ventilation of the entire source. An additional forced ventilation of the outer hemisphere inclosure is necessary to carry away the large quantity of heat generated by the lamps. For this purpose a low-pressure supply of filtered air (sec. III, 4) is delivered through the opening (65) into the hollow base compartment of the instrument. The course of the air stream into the horseshoe-shaped compartment (32) is indicated by arrows (65). A section through this compartment is shown in the upper part of the figure. It extends continuously around the door carrying the milk-glass hemisphere and sample holder and through the different base plates of the instrument. From this compartment the air enters the hemisphere inclosure through nine holes (33) in the casting (31), and leaves through the many annular openings around the bases of the lamps. The air stream is thus most effective in the cooling of the lamps.

3. PHOTOMETRIC EQUIPMENT

The intensity and polarization of the S-beam, as taken from the sample under either type of illumination, is measured by direct comparison with the intensity and polarization of another beam, called the C-beam, which originates at separate constant comparison sources especially designed to accompany each illumination unit. The intensity of the C-beam may be varied in known manner until it becomes equal to that of the S-beam. The device employed for this purpose is called the variometer; that employed to bring the two beams into the proper position for direct comparison is called the comparator. The photometer is a combination of comparator and variometer with a light-sensitive receiver, which in the present equipment is the human eye. An important element of a comparator for visual photometry is the photometric field, where a criterion for the

equality of intensities of the S- and C-beams is established. In the present equipment two different criteria for this equality are provided, as employed respectively in the well-known equality-of-brightness and minimum-flicker methods of photometry.

In the equality-of-brightness method a two-part photometric field is used, one part being illuminated by the S-beam and the other part

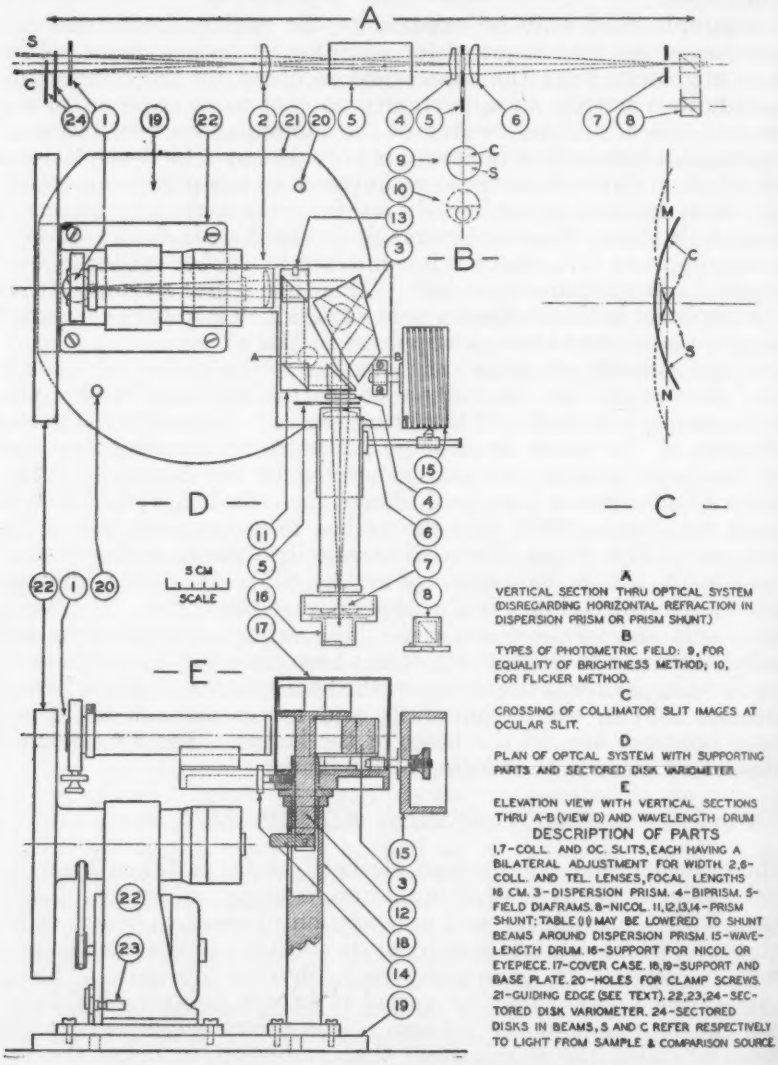

FIGURE 8.—*Comparator and sectored-disk variometer.*

by the C-beam. The equality of intensities is indicated by an equality of brightnesses between the two parts of the field with accompanying disappearance of the dividing line. In the minimum-flicker method a one-part photometric field is used, illuminated alternately by the S- and C-beams. The alternations cause a brightness flicker in the

field which, with proper adjustment of the frequency of the alternations, is reduced to a sharp minimum when the alternate brightnesses of the photometric field, and hence the intensities of the S- and C-beams, are the same. This provision for the use of the minimum-flicker method avoids the uncertainty of equality-of-brightness settings when the two parts of the photometric field differ in chromaticity; for, when the required flicker frequency adjustment is made the chromaticity difference disappears leaving only a residual brightness flicker.

In the present equipment the comparator is constructed to include the dispersion prism, lenses, and slit system of an ordinary spectrometer, so that beams of small wave-length extension may be filtered from the composite S- and C-beams. If the spectral filter is not required, then the dispersion prism is effectively removed by a prism shunt, and ordinary light filters may be employed to sort out desired components of the composite beams. In addition to these provisions for the control of spectral conditions, a nicol prism may be employed to separate like polar components from each beam. This provision is required in polarization measurements and in some intensity measurements. Detailed description of the photometric equipment is given in the following sections:

(a) COMPARATOR AND SELECTIVE LIGHT FILTERS

The passage of the S- and C-beams through the optical parts of the comparator is shown in views A and D of figure 8. The instrument is essentially a spectrometer equipped with a constant deviation dispersion prism (3) and a prism shunt (11, 12, 13, 14). A biprism (4) mounted over the telescope lens (6) is the essential element added to the original instrument to convert the device into a comparator.[8]

The dispersion system of the instrument (parts 1, 2, 3, 6, and 7) selects any desired homogeneous component from the composite entrant beams. When the diffusive and absorptive properties of the sample are to be measured directly for some fixed condition of composite illumination (table 1), the dispersion prism is effectively removed from the optical system by insertion of the prism shunt, which is shown in views D and E of figure 8. By loosening set screw (14) the circular plunger (12) may be lowered until the three total-reflection prisms on table (11) intercept the beams emerging from lens (2) and direct them around the dispersion prism to the biprism. A vertical guide bar (13) prevents any rotation of the prism table. The prisms are readily adjusted so that this change is made without appreciable shifting of the paths of the entrant beams. When the prism shunt is used light passes through the instrument with but slight alteration in spectral distribution. Suitable glass or liquid light filters may be inserted in the beams at any convenient position before the eye. This completes the arrangements for effective control of the spectral conditions of illumination on the sample.

By inserting a nicol prism before the emergent slit of the comparator only the corresponding polar component of each entrant beam eventually reaches the eye. The nicol is mounted in a cylindrical tube (8) which may be inserted in the projecting tube (16). A pin on the

[8] This form of biprism spectrocomparator, when used with the sectored-disk variometer (22, figure 8), is essentially the arrangement employed in the Keuffel and Esser spectrophotometer. See C. W. Keuffel J. Opt. Soc. Am. & Rev. Sci. Instr. 11, 403 (1925).

nicol tube fits a slot in the holder tube so that the principal plane of the nicol may be oriented accurately in vertical and horizontal positions. Hence measurements of the polarization of the S-beam are made only with reference to vertical or horizontal planes. For a majority of the measurements on different samples the vertical reference plane will be perpendicular to the plane of incidence for unidirectional illumination, and always perpendicular to the plane of observation with the hemisphere source. Generally the vertical or horizontal plane will be the principal plane of polarization for the S-beam. This is not always the case, however, particularly for materials such as textile fabrics having structural features varying with direction on the surface.

Upon looking through the emergent (or ocular) slit (7) of the comparator one sees the uniformly illuminated surfaces of the biprism. The field of view, called the photometric field, is limited by the form and size of the diaphragm aperture (5). In the equality-of-brightness method of photometry a large circular aperture is used which exposes equal areas of each inclined face of the biprism, as shown at (9) in view B, and subtends an angle of approximately 5.5 degrees at the ocular slit. The photometric field is thus divided into two equal semicircular parts by the sharp horizontal line of intersection of the biprism faces. The two entrant beams pass, respectively, one through each inclined face of the biprism and thence through the emergent slit (and nicol) to the eye. In the minimum-flicker method of photometry the one-part photometric field is limited by a small circular aperture, which is shown at (10) in view B and subtends an angle of 2 degrees at the ocular slit. This aperture is eccentric with respect to the axis of the lens system and exposes to view only a part of one face of the biprism. The paths of the S- and C-beams must therefore be exactly superposed in their passage through the instrument. Optical arrangements for this purpose are described in (sec. 3 (d)).

The brightnesses of the adjacent parts of the photometric field in the one method, or the alternate brightnesses of the same part of the field in the other method, are proportional respectively to the intensities of the corresponding entrant beams, or to the particular homogeneous, composite, or polar components of the beams which are being transmitted by the comparator to the eye. In both methods the intensity of the C-beam relative to that of the S-beam, is controlled by the variometers described below, until the respective criterion for equal field brightnesses is satisfied. The intensity ratio is then given by the variometer reading, with due regard to the polarization of the entrant beams as considered in section IV.

The comparator is mounted on the base plate (19), along with the sectored-disk variometer (sec. 3 (b)), so that the combination may be transferred readily from one illumination unit to the other. It is shown in proper position with each unit in figures 3, 4, and 5. The exact position of the photometric unit in the base plates of either illumination unit is determined by the straight edge (21), figure 8,

which is pushed snugly against a corresponding edge on the base plate of each illumination unit. The exact position of the instrument parallel to this edge, which is parallel to the paths of the entrant beams, is relatively unimportant.

(b) SECTORED-DISK VARIOMETER

The sectored-disk variometer [9] is a combination of two sectored disks, each with two 90° apertures, and rotating in the same direction with equal angular velocity. One of these disks is larger in diameter than the other and cuts the S- and C- beams, as illustrated at (24) in figure 8. The other disk cuts the C-beam only. The phase angle between the rotating disks may be varied continuously so that the ratio of the total aperture of the combination of disks to the aperture of the single outer disk varies continuously from zero to unity, with a corresponding continuous variation in the relative (time-averaged) intensities of the entrant beams. The intensity ratio is read directly on the instrument scale.

The device is mounted so that both disks may be lowered slightly until the two disks cut the C-beam only. This operation doubles the scale reading of the instrument and doubles the field brightness in the comparator corresponding to a given intensity of the S-beam. The transmission range of the instrument now extends from 0 to 0.5, but the greater field brightness and more open scale are advantageous in the measurement of low intensities.

(c) COMPARISON SOURCES

Upon reference to the general plan of the equipment in figure 2, it is seen that the C-beam is taken from the interior surface of either of two lamp inclosures (designated as comparison sources), depending on the particular illumination unit with which the comparator is being used. In either case the observed portion of the interior surface is removable, permitting the C-beam to be taken instead from the interior surface of a hollow sphere. This sphere is part of the inverse-square variometer (sec. 3 (e)).

The right-hand diagram in figure 9 shows the construction of the comparison lamp inclosure used with the diffused illumination unit. With the lamps operating at normal voltage the brightness of the interior surface is approximately the same as the interior brightness of the milk-glass hemisphere. Hence the brightness of this comparison source is always equal to or greater than the brightness of a sample under the hemisphere illumination. The left-hand diagram in figure 9 shows the construction of the comparison lamp inclosure used with the unidirectional illumination unit.

The construction principle for both of the comparison sources is the same. The lamps are placed in a small inclosure with walls of

[9] See detailed description of similar instruments by C. W. Keuffel, J. Opt. Soc. Am. and Rev. Sci. Instr. II, 403(1925).

high reflectance and good diffusing power. Hence, the greater part of the illumination of the interior wall is the diffused light multiply

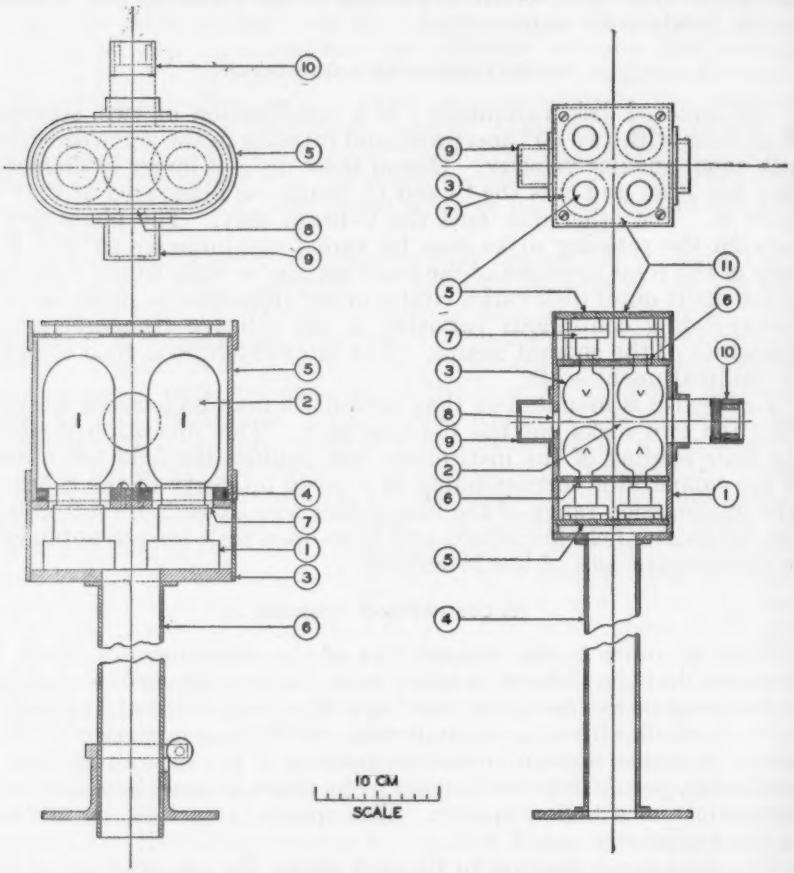

FIGURE 9.—*Construction of comparison sources*

A.—Right-hand source used with diffused illumination unit.

1. Aluminum box. *2, 3.* Cubical compartment containing bulbs of 8 lamps of same type as hemisphere lamps, figure 7. Interior surface of compartment heavily coated with magnesium oxide. *4, 5.* Brass tube support and holes through which a forced draft of air is supplied for ventilation. *6.* Bases of lamps project through circular holes in top and bottom of cubical compartment. Annular openings about lamp bases serve for ventilation purposes. *7.* Lamp receptacles. *8, 9.* Apertures for C-beam to comparator. *10.* Removable circular portion of back wall, from which C-beam to comparator is taken. *11.* Top of box, with upper 4 lamps, is removable for inspection or renewal of lamps.

B.—Left-hand source used with unidirectional illumination unit.

1. Mogul lamp receptacle. Upper portion of porcelain body cut away for better cooling of lamp base. *2.* Lamp units up to 1,000 watts may be used. *3.* Support for lamps receptacles. *4.* Asbestos plate. Upper surface smoked with magnesium oxide. *5.* Sheet-iron shell with removable top. Inner surfaces coated with white porcelain enamel and smoked with magnesium oxide. Shell fits snugly over asbestos plate and is readily removed for renewal of lamps. *6.* Supporting brass tube through which a forced draft of air is supplied for cooling purposes. *7.* Annular opening about base of lamp for ingress of air to lamp inclosure. *8, 9.* Apertures in front wall of lamp inclosure for passage of C-beam to comparator. *10.* Removable circular portion of the back wall, from which the C-beam to comparator is taken.

reflected within the inclosure. The lamps are symmetrically arranged with respect to the emergent C-beam. Thus a source of

uniform brightness over an extended area is obtained with no appreciable polarization of the C-beam to the comparator. Moreover, small lateral displacements of this beam do not appreciably alter its intensity.

(d) FLICKER-DISK ATTACHMENTS

In the use of the minimum-flicker method of photometry, provision must be made for a rapid periodic substitution of the C-beam for the S-beam in the comparator. This substitution is effected with the flicker-disk attachments which form accessory parts of each illumination unit.

By reference to figure 7 it is seen that the path of the S-beam is direct and horizontal from the sample to the entrant slit of the comparator. The path of the C-beam from the comparison sources is turned downward at prism (7) and intersects the path of the S-beam at 90°. A polished metal disk with two 90° open sectors is placed at the intersection of the beams so that the upper mirror surface of the disk contains the point of intersection of the axes of the beams and is inclined at 45° to each axis. By rotation of the disk the C-beam is periodically substituted for the S-beam whenever a closed sector of the disk intersects the beams.

By reference to the unidirectional illumination unit in figure 4, the paths of the S- and C-beams from the sample and comparison sources may be followed. A small flicker disk (47) is inserted at the intersection of the beams in a manner similar to that described for the diffused illumination unit. The principle of operation is precisely the same as before.

When the minimum-flicker method is used the diaphragm slide (5) of figure 8 is moved so that the field of view is limited by the circular aperture (10), and the sectored-disk variometer (22, 24) is set with open sectors permitting free passage of the beams to the comparator. The equality of intensities is effected by use of the inverse-square variometer.

(e) INVERSE-SQUARE VARIOMETER

In the minimum-flicker method of photometry a sectored-disk variometer is inapplicable because of the obvious introduction of stroboscopic effects. The variometer commonly employed in this case is based on the inverse-square law of photometry, and consists essentially of a lamp suitably mounted on a track so that its distance from a diffusion screen may be varied continuously. Assuming that certain conditions, considered below, are fulfilled to a sufficient approximation, then the brightness of the diffusion screen, by reflected or transmitted light, is proportional to the inverse square of the distance between the lamp and the screen. The screen thus serves as a continuously variable secondary source of light for the comparison beam to the photometer.

The inverse-square variometer used with the present equipment is outlined in figure 2. Two spherical diffusion screens are provided, each formed by the interior surface of a hollow white-lined sphere. The spheres are placed one at each end of the lamp track, and each sphere serves as a variable comparison source for separate use with

the flicker-disk attachment of the corresponding illumination unit. Inasmuch as the construction of both ends of the variometer is the same, only one end of the instrument is shown in figure 10. The C-beam is taken from the interior magnesium-oxide surface of the sphere (3). Lamp (8) is movable along track (11) and its light

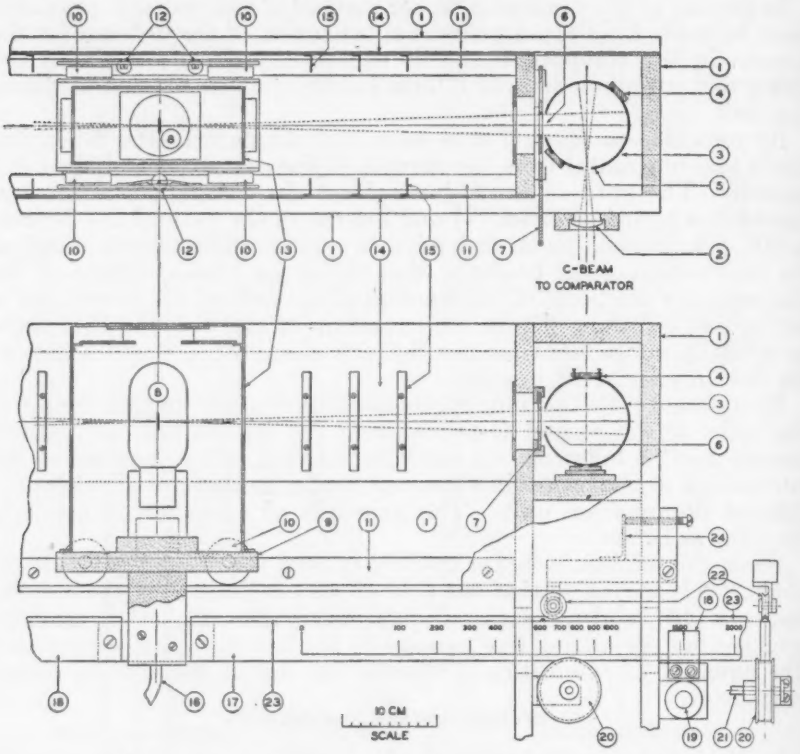

FIGURE 10.—*Construction of inverse-square variometer.*

1. Wood frame. *2.* Lens (with lens 6 of figure 7) focusing comparator slit approximately in plane of aperture in sphere (3), thus permitting use of small aperture. *3, 4.* Iron sphere 95 mm in diameter, built up of two hemispheres and a supporting iron ring (4). Inner surface of sphere coated with white porcelain enamel and smoked with magnesium oxide. *5.* Aperture for C-beam, diameter 6 mm. *6.* Aperture for entrant beam to sphere, diameter 22 mm. *7.* Brass slide having three apertures of different diameter, any one of which may be placed before sphere aperture (22). Areas of apertures are in the proportion of 10:5:1. *8.* 400-watt projection lamp, with plane of lamp filaments parallel to plane of aperture into sphere. *9.* Lamp carriage. *10.* Roller skate wheels. *11.* Track for lamp carriage made of one-inch angle iron and screwed to sides of wood frame. *12.* Small wheels rolling against vertical side of angle-iron track, thus preventing the scraping of carriage against side of track. *13.* Lamp box. *14, 15.* Blackened metal fins preventing reflection of light from sides of frame into sphere. *16.* Flexible current leads. *17.* Seasoned wood driving bar attached to lamp carriage. Heavy white paper is glued to sides of bar and one side ruled with a distance-squared scale. *18, 19.* Pointer and lamp for reading scale. *20.* Rubber-tired drive-wheel for bar (17). *21.* Shaft connecting drive wheel with hand wheel, which is placed within convenient reach of observer. *22.* Guiding pulley rolling on angle brass strip (23). *23.* Angle brass strip screwed to upper flat edge of (17), thus guiding motion of bar. *24.* Spring brass providing downward tension on (22).

admitted to the sphere through any one of three circular apertures in slide (7). The largest aperture is 20 mm in diameter and the areas of the three apertures are in the proportion of 10:5:1. These apertures are made accurately and calibrated mechanically.

The intensity of the C-beam to the comparator is proportional to the total quantity of light projected into the sphere, which in turn is proportional to the area of the effective entrant aperture and to the

inverse square of the distance between the plane of the lamp filaments and the plane of the aperture. The accuracy of this law for the lamp track and spherical diffusion screen was tested [10] by comparison with the scale of the sectored-disk variometer, which had been calibrated previously by use of standard sectored disks of accurately known aperture. It was found that for each aperture into the sphere, and for lamp positions down to 15 cm from the aperture, no departure from the inverse-square law was indicated by the photometric measurements, the uncertainty of which is estimated as 1.5 percent. Also, when the three different apertures were used successively, with the lamp fixed at distances of 50 and 20 cm from the sphere, the relative intensities of the C-beam were in each case with the same degree of accuracy in the proportion of 10:5:1.

The spherical diffusion screen, with its variable entrant aperture, affords a convenient and accurate means for extending the intensity range of the lamp track. The arrangement replaces the plane reflection or transmission types of diffusion screen and the approximately neutral light filters commonly employed in this type of variometer. The apertures are, of course, strictly nonselective in their spectral transmission, so that the relative spectral distribution of light in the C-beam remains constant over the entire intensity range of the variometer. This is a very desirable feature of the instrument.

Another reason for the use of this type of diffusion screen with the present equipment is that an extended source of the highest possible brightness is desired with no polarization in the C-beam to the comparator. The spherical screen fully fulfills the polarization condition, the advantage of which is explained in section IV. A plane magnesium carbonate reflection screen would yield a comparable intensity of the C-beam but then the beam would be partially polarized. The polarization condition could be fulfilled with a plane transmission screen such as milk-glass; but, if this screen is a sufficiently good diffusor so that the inverse-square law of the instrument is accurate,[11] then its transmission is likely to be so low that the spherical screen gains the intensity advantage. A thorough quantitative investigation of this point has not been made. It is possible that entrant apertures of larger diameter could be used with the sphere, thus increasing the collection of light from the lamp.

4. VENTILATION SYSTEM

Of the five different light sources provided with this equipment, the track lamp (8, fig. 10) is self-ventilating, and a forced ventilation has been described for the unidirectional illumination source. The hemisphere source for completely diffused illumination, and the two comparison sources (fig. 9), each contain lamps in an inclosure, the interior surface of which is coated with magnesium oxide.

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[10] For this test the S-beam to the comparator was taken from a magnesium carbonate surface illuminated by a 400-watt lamp. This lamp was operated in series with the 400-watt track lamp, and the current held constant during the test. The relative intensities of the C-beam for different positions of the track lamp could then be measured with the sectored-disk variometer and the result compared with values computed by the inverse-square law.

[11] The diffusion screen of whatever type must be a suffcient approximation to the ideal perfect diffusor that the intensity-direction gradient in the neighborhood of the mean direction of observation remains sensibly constant as the distance of the lamp from the screen is changed. The permissible degree of departure of the screen from the perfect diffusor depends on the degree of approximation of the illumination on the screen to the ideal unidirectional condition. It is of interest to note that the perfect diffusor and strictly unidirectional illumination are both ideal concepts which can be approached without limit but are never exactly realized. Consequently, the law of the inverse-square variometer can be made to operate to any desired degree of accuracy by proper choice of above-mentioned conditions.

It has been found necessary to filter the air used for the ventilation of such inclosures in order to remove dust and dirt which otherwise would be deposited on the white reflecting surfaces and thus appreciably reduce their reflectance. This is particularly undesirable in the hemisphere source, for the uniformity and constancy of the reflectance over the surfaces is of importance in maintaining the desired condition of illumination on the sample. Likewise, air used for direct cooling of the sample in the diffused-illumination unit must be cleaned before being used in order to prevent the deposition of dirt on the sample or standard.

The construction of air filters and their connection to the light sources is clearly depicted in figure 11. Each filter consists of a few overlapping layers of absorbent cotton, held in place between two wood frames, which are covered with coarse-mesh wire screening. The high-velocity air jet for cooling the sample (see parts 57, 58, 59,

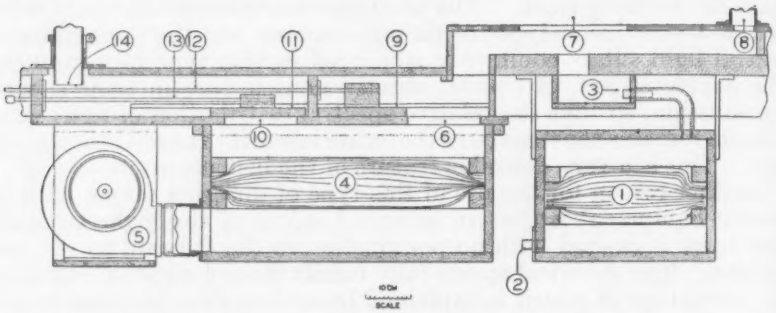

FIGURE 11.—*Construction of ventilation system*

1. Air filter consisting of three or four layers of absorbent cotton. *2.* High-pressure air inlet. *3.* Connection to diffused illumination unit for high-velocity air jet on sample. (See fig. 7, pts. (59) and (60).) *4.* Air filter for low-pressure large-volume supply to hemisphere (fig. 7) and to comparison lamp sources (fig. 9). *5.* Blower. *6.* Outlet to (7) and (8). *7.* Air passage to hemisphere source. Connects with compartment (32) of figure 7. *8.* Air passage to comparison source for diffused illumination unit. See arrow (66) of figure 7 and right-hand diagram of figure 9. *9.* Sliding door to close passage (6). *10, 11.* Sliding door to open passage (10) when air supply is needed for ventilation of comparison source used with unidirectional illumination unit. See left-hand diagram of figure 9. *12, 13.* Rods to operate doors (9) and (11). *14.* Air passage to comparison source. See figure 9, left, part (6).

and 60, figure 7) is supplied through filter (1), figure 11, from the laboratory compressed air supply. A larger volume of air at lower pressure is supplied by the blower (5) through the larger filter (4). This serves for the ventilation of the hemisphere and comparison sources.

IV. INTENSITY AND POLARIZATION MEASUREMENTS

In the preceding description of the equipment and its operation a given homogeneous, composite, or polar component of the S-beam is always compared directly with a corresponding or a fixed component of the C-beam, the intensity of which can be varied in a definitely determined manner. The suggested procedure in the measurements would imply that the absolute intensity of any component of the C-beam is known in terms of some fixed intensity unit. This is not the case, however, and hence it is necessary to apply a substitution method as the standard photometric procedure in intensity measurements.

In the substitution method the intensity of the S-beam with the sample in place is compared with the intensity of the S-beam from a standard material, when the standard is subjected either to the same conditions of illumination as the sample or to some other definitely specified conditions. If the diffusive and absorptive properties of the standard are known, then the corresponding properties of the sample are determined. In the application of the method the standard is alternately substituted for the sample and each compared successively with the comparison source, so that the C-beam thus serves only as a means for balancing intensities of the S-beam from sample and standard, respectively, and the properties of the comparison sources are thus eliminated from the final results of the measurements.

Under various conditions of illumination many materials introduce a considerable degree of polarization in the light reflected or transmitted to the photometer. In the general photometric procedure to be described it is assumed at first that the polarizing properties of

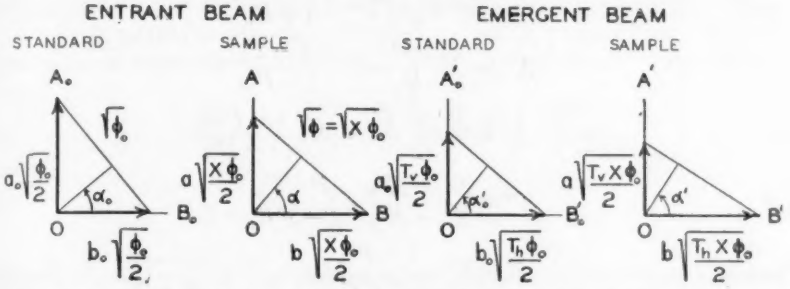

FIGURE 12.—*Polar analysis of light beams, before and after passage through the comparator*

$\phi \equiv$intensity; $P \equiv$polarization; $a^2+b^2=2$. $P \equiv [(OA)^2-(OB)^2] \div [(OA)^2+(OB)^2] = 0.5\ (a^2-b^2) = \cos 2\ \alpha$. $a^2=1+P$; $b^2=1-P$; $-1 \leq P \leq 1$

the sample are to be measured along with the spectral or directional intensity distributions of reflected or transmitted light. The discussion will apply equally well to the measurement of homogeneous or composite components of the S-beam and in the use of either type of variometer in either the equality-of-brightness or minimum-flicker methods of photometry. The polarization of the S-beam is herein measured with reference to a vertical plane. This reference plane is most significant in a later discussion of polarization errors and will be approximately coincident with, or perpendicular to, the principal plane of polarization of the S-beam for the majority of measurements that may be required in various applications of the equipment.

Let Φ_0 and P_0 represent, respectively, the intensity and polarization of the S-beam, when this beam is taken from the surface of the standard. Let $X\Phi_0$ and P represent the corresponding quantities when the sample is substituted for the standard. The factor X is the brightness ratio of sample to standard and is the quantity to be derived from the variometer readings. The polar analysis of the S-beam, as taken from the sample or standard, is given in the left half of figure 12. The vertical and horizontal vectors represent, respectively, the amplitudes of the vertical and horizontal polar components of intensity.

Let T_v and T_h represent, respectively, the transmissions of the comparator for the vertical and horizontal polar components of the S-beam. All factors determining the transmission of the instrument affect the two components equally, with the exception of reflection phenomena at the surfaces of the dispersion prism. As described by the Fresnel reflection laws the horizontal polar component at these surfaces is more copiously transmitted than the vertical component. The polar analysis of the S-beam after emergence from the ocular slit of the comparator is represented in the right half of figure 12. When the principal plane of the nicol is set vertical or horizontal, then only the corresponding polar component of the S-beam is transmitted through this prism to the eye.

Let X'_v be the ratio of variometer readings for the vertical polar components of the S-beam, as received from the sample and standard, respectively. Let X'_h denote the corresponding ratio for the horizontal polar components. Then, by figure 12,

$$X'_v = X \cdot \frac{a^2}{a^2_o} = X \cdot \frac{1+P}{1+P_o}. \tag{1}$$

$$X'_h = X \cdot \frac{b^2}{b^2_o} = X \cdot \frac{1-P}{1-P_o} \tag{2}$$

Let
$$X' \equiv \frac{X'_v + X'_h}{2} = X \cdot \frac{1-PP_o}{1-P^2_o} \tag{3}$$

and
$$P' \equiv \frac{X'_v - X'_h}{X'_v + X'_h} = \frac{P-P_o}{1-PP_o} \tag{4}$$

Then
$$X = X' \cdot \frac{1-P^2_o}{1-PP_o} \tag{5}$$

$$P = \frac{P'+P_o}{1+P_oP'} \tag{6}$$

These formulae show how, in the substitution method, the polarizing properties of the sample and standard enter into the required intensity and polarization measurements. The same formulae will apply, of course, when the substitution method is not employed, for then the C-beam would take the place of the S-beam from the standard, and P_o would represent the initial polarization of the C-beam. It is more convenient when only polarization, or only relative directional distributions of light are measured, to eliminate the use of the standard and to employ the more direct comparison method of photometry. It is for this purpose that care was taken in the design of all comparison sources to have the initial polarization of the C-beam zero. Likewise, in the use of the substitution method, it is important to choose experimental conditions such that the initial polarization P_o of the S-beam from the standard is negligible. Then, directly, $X=X'$, and $P=P'$. To fulfill this condition a uniform and optically isotropic diffusing medium is chosen for the standard. Under completely diffused illumination it may always be observed normal to its surfaces for reflected or transmitted light. Under unidirectional normal illumination it may also be observed

normal to its surfaces by transmitted light. Under such symmetrical conditions of illumination and observation the polarization, P_o, will be negligible or zero.

It is seen that the general photometric procedure in the intensity or polarization measurements calls for separate measurements of mutually perpendicular polar components and the combination of such measurements in equations (3), (4), (5), and (6). In the majority of the applications of this equipment, however, a determination of the polarizing properties of materials is not required. In such event the intensity measurements may be simplified by direct measurement of the whole intensity of the S-beam (nicol removed), provided certain additional conditions are fulfilled. In consequence of the polarizing action of the dispersion prism the transmission of the comparator depends on the state of polarization of the entrant beams, and appreciable errors in the intensity measurements may result if the variable polarization of the S-beam is disregarded.

Let it be assumed that the nicol is removed from the optical system of the comparator so that the whole intensity of the S-beam, unresolved into polar components, is to be measured directly by either of the photometric methods provided. Let X' represent, as before, the ratio of variometer readings. Then, by reference to figure 12, we have

$$X' = X\,\frac{(a^2T_v + b^2T_h)}{(a^2{}_oT_v + b^2{}_oT_h)} = X\cdot\frac{1+PP_t}{1+P_oP_t}$$

or

$$X = X'\,\frac{1+P_oP_t}{1+PP_t} \tag{7}$$

where $P_t = \dfrac{T_v - T_h}{T_v + T_h}$ is the polarization introduced by transmission of light through the comparator with dispersion prism.

Let ΔX be the difference between the true brightness ratio X and the value X' given by the variometer readings. Then the fractional error in the brightness ratio, which would result if the polarization of the beams were disregarded, is

$$\frac{\Delta X}{X} = \frac{X'-X}{X} = \frac{(P-P_o)P_t}{1+P_oP_t} \tag{8}$$

It is seen that there are two conditions for which the error is zero. The polarization P_t is practically all introduced by the dispersion prism of the comparator; hence in all nonspectral measurements, wherein the prism shunt is used, $P_t = 0$ and the polarization error is zero. Likewise, when the polarization of the beams from the sample and standard are the same, then $P = P_o$.

When the conditions of measurement are chosen such that the polarization of the beam from the standard is always zero, then $P_o = 0$ and $X = X'/(1+PP_t)$, so that

$$\frac{\Delta X}{X} = PP_t \tag{9}$$

Having the refractive index of the dispersion prism material for different wave lengths, the spectral transmission of the prism (disregarding

absorption in the prism glass) has been computed by means of the Fresnel formulae for the vertical and horizontal polar components of the entrant beams. These components are perpendicular and parallel, respectively, to the plane of incidence on the dispersion prism. From the values of T_v and T_h thus obtained, the fractional polarization P_i was computed. The data are shown in table 2.

TABLE 2.—*Polarization introduced by the dispersion prism*

Wave length (mμ)	Transmission of prism by Fresnel formulas		Polarization P_i	Wave length (mμ)	Transmission of prism by Fresnel formulas		Polarization P_i
	T_h	T_v			T_h	T_v	
420	0.9947	0.5317	−0.365	580	0.9993	0.4748	0.312
460	.9971	.5104	.344	620	.9995	.4678	.306
500	.9983	.4951	.330	660	.9998	.4621	.301
540	.9990	.4840	.320	700	.9999	.4576	.297

It is seen that the mean value of P_i throughout the spectrum is approximately −0.32. Thus a 31 percent polarization of the S-beam from the sample would result in an error of 10 percent in the direct measurement of the brightness ratio X of sample to standard.

In the usual methods of spectrophotometry the sample and standard are observed simultaneously under equal illumination from the same source and the C-beam is taken directly from the surface of the standard. The above analysis applies identically to this case and P_o is then the polarization of the C-beam.

WASHINGTON, June 26, 1934

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THE SYSTEM: PbO–SiO_2

By R. F. Geller, A. S. Creamer, and E. N. Bunting

ABSTRACT

The system PbO–SiO_2, of interest to investigators and manufacturers of ceramic glazes and glasses, was investigated. The following compounds were identified and their optical properties, linear thermal expansion, and melting temperatures determined: $4PbO.SiO_2$, $2PbO.SiO_2$, and $PbO.SiO_2$. The compositions and melting points of three eutectics were determined also.

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I. INTRODUCTION

The study of this system was preliminary to a study of the system K_2O–PbO–SiO_2, the purpose being to provide information of fundamental nature to manufacturers and investigators of ceramic glazes and glasses.

Much of the earlier data for the PbO–SiO_2 system is incomplete and often conflicting.[1] The most comprehensive report is that by Krakau and Vachrameev, who found maxima at 744 C and 765 C, corresponding to the compounds $2PbO.SiO_2$ and $PbO.SiO_2$, and who give detailed results of exhaustive petrographic studies. They suggest, but failed to identify, the compounds $3PbO.SiO_2$ and $3PbO.2Si_2O_2$. The latter would correspond to the mineral barysilite.

[1] H. C. Cooper, L. I. Shaw, and N. E. Loomis; Am. Chem. J. 42, 461 (1909); S. Hilpert and P. Weiler, B. d. Deut. Ker. Gesell. 42 [III], 2969 (1909); S. Hilpert and R. Nacken, B. d. Deut. Ker. Gesell. 43 [II], 2565 (1910); H. C. Cooper, E. H. Krause and A. A. Klein, Am. Chem. J., 47, 273 (1912); K. A. Krakau and N. A. Vachrameev, Keram i Steklo, 8, [1], 42 (1932).

II. PREPARATORY WORK

1. PREPARATION OF MIXTURES

The "end members" used in preparing the various mixtures were PbO (sublimed litharge) containing 0.02 percent total detected impurities,[2] and SiO_2 (quartz crystal) crushed to pass a no. 100 sieve and purified. It contained 0.02 percent nonvolatile residue on evaporation with HF and H_2SO_4.

All fusions were made in platinum, using electrically heated furnaces. For each "key" mixture the proper proportions of PbO and SiO_2 were mixed intimately and fused. By using temperatures only slightly higher than required for complete melting, and by repeated grinding and remelting instead of prolonged heating, it was possible to prepare microscopically homogeneous melts without detectable volatilization of PbO.[3] These key mixtures were analyzed chemically and were used in various combinations to produce mixtures of intermediate composition.

2. CHEMICAL ANALYSES

The PbO content was determined as sulfate by double evaporation with HF and H_2SO_4, and also electrolytically by dissolving the sample in diluted HNO_3, depositing on platinum gauze, drying at 110 C, and using the previously determined factor of 0.931 to calculate the equivalent PbO. With few exceptions, results by these two methods agreed within 0.1 percent. It was established by test that the SiO_2 content could be determined satisfactorily by difference.

3. IMMERSION MEDIA

All of the compounds in this system, and also the PbO, have indices of refraction above the highest attainable with liquid immersion media. Solid media, ranging in index of refraction from 1.74 to 2.58 were available from a previous investigation.[4] However, their indices were redetermined by means of a reflecting goniometer. White light passed through a no. 25 Wratten filter provided the illumination for the calibration of the immersion media.

III. EXPERIMENTAL PROCEDURE

1. HEATING CURVES AND QUENCHES

The thermal studies were made by the well established quenching method [5] supplemented, in most cases, with heating curves by the differential thermocouple method.

All compositions in which PbO is the primary phase were prepared for thermal study by fusing portions of previously prepared mixtures, quenching in water, and then crystallizing slightly below the solidus temperature. This procedure was necessary because equilibrium was

[2] Furnished by the Eagle-Picher Lead Co., and analyzed by the chemistry division of the National Bureau of Standards for Cu (0.002 percent), Bi (0.018 percent), Fe (less than 0.001 percent), and for Zn, Ni, and Mn which were not detected.

[3] Olaf Andersen, J. Amer. Cer. Soc. 2 [10], 784 (1919).

[4] L. T. Brownmiller, The Amer. Mineralogist 12, 43 (1927).

[5] E. S. Shepherd and G. A. Rankin; Am. J. Sci. 28,293(1909). F. C. Kracek, N. L. Bowen and G. W. Morey; J. Phys. Chem. 33,1857(1929).

not attained in these mixtures, when cooled slowly from the liquid state, due to the PbO crystallizing in large plates characteristic of this oxide. For this reason, and also because mixtures containing more than 8 to 10 percent SiO_2 by weight crystallize very slowly, it was found advisable to study all compositions by determining heating (rather than cooling) curves, and by using for quenching tests specimens of material which had first been completely crystallized and then held at the desired temperature for 15 min or more prior to quenching. The time required to complete crystallization varied from a few minutes to several days, increasing rapidly as the ratio of SiO_2 to PbO increased. PbO, for example, crystallized so rapidly that it could not be obtained as a glass while the crystallization of the $PbO.SiO_2$ composition required 2 days or more, depending on the crystallizing temperature.[6]

For the differential thermocouple method two average heating rates were used, 0.9° C and 1.8° C per min. Holding at constant temperatures (±0.5° C), or changing temperatures at a predetermined rate, was accomplished with automatically controlled furnaces. The type of control used is described in principle by Adams.[7] Pt to Pt–Rh thermocouples were used for all temperature measurements and were calibrated periodically by using the inversion temperature of K_2SO_4 (583 ± 1° C), or the temperature of melting of either K_2SO_4 (1069.1 C) or KCl (770.3 C),[8] as reference points.

2. LINEAR THERMAL EXPANSION

Determinations of linear thermal expansion were made by the interferometer method [9] using an average heating rate of from 2.0° to 2.5° C per min, and chromel-alumel thermocouples for measurements of temperature.

3. MICROSCOPIC EXAMINATIONS

The petrographic microscope was used to determine the phases present in the quenched samples.[10] Identification of crystal phases was limited practically to the establishment of their optical character and also their indices of refraction which are believed to be accurate to ±0.01. White light passed through a no. 25 Wratten filter provided the illumination for observation of the quenched samples.

IV. RESULTS

1. COMPOUNDS

Three compounds were found in the system: $4PbO.SiO_2$ $2PbO.SiO_2$, and $PbO.SiO_2$.

$4PbO.SiO_2$, *tetralead silicate.*—This compound melts incongruently to form PbO and liquid at 725 ± 1° C and is a final product of crys-

[6] S. Hilpert and R. Nacken, see footnote 1 on p. 237.
[7] J. Opt. Soc. Am. 9,599(1924).
[8] H. S. Roberts, Some New Standard Melting Points at High Temperatures; Phys. Rev. 2, [23] 386(1924).
[9] G. E. Merritt, BS J.Research 10,59(1933);RP515.
[10] E. S. Larsen and H. Berman, U.S. Geol. Sur. Bull. 848(1934).

tallization in all mixtures containing up to 33.33 mol percent (11.85 wt percent) SiO_2. It crystallizes readily and apparently occurs in 3 forms. The α form, stable above $720 \pm 1°$ C, crystallizes as irregular plates of high birefringence and is characterized by the clear blue to violet color, under crossed nicols, when the plates lie normal to the axis of the microscope. It is biaxial positive with an optic angle about 40°. The approximate indices of refraction are $\alpha = 2.31$, $\beta = 2.34$, $\gamma = 2.38$. The β form, stable between about 155 and 720 C, was not distinguished optically from the γ form, stable below about 120 C, except by relative birefringence. Specimens crystallized at or below 720 C appear as minute, probably prismatic, grains of medium birefringence and average index of refraction approximating 2.34.

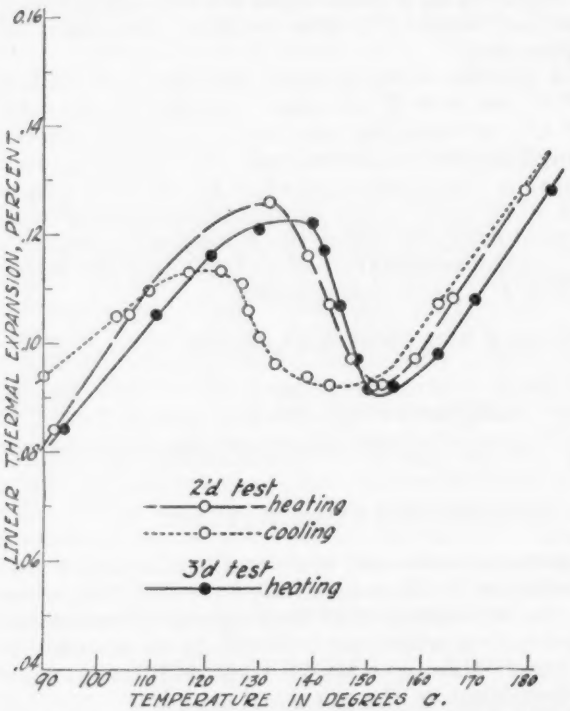

FIGURE 1.—*The linear thermal expansion of* $4PbO.SiO_2$ *showing reversal caused by crystal transformation.*

$2PbO.SiO_2$, *lead orthosilicate.*—This compound melts congruently at $743 \pm 3°$ C. It is the primary phase in mixtures containing approximately 25 to 40.5 mol percent (8.22 to 15.4 wt percent) SiO_2 and crystallizes in well-defined prismatic form with a characteristic cleavage normal to the prismatic axis. The extinction is parallel, the character biaxial negative, and the optic angle about 80°. Approximate indices of refraction are: $\alpha = 2.13$, $\beta = 2.15$, $\gamma = 2.18$.

$PbO.SiO_2$, *lead metasilicate.*—This compound melts congruently at $764 \pm 3°$ C. It is the primary phase in mixtures containing approximately 40.5 to 61.0 mol percent (15.4 to 29.6 wt percent) SiO_2. Crystals appear prismatic when formed in glass containing an excess of SiO_2, but otherwise are of indefinite form. They are biaxial negative, optic angle about 60°, birefringence medium, and average index of refraction about 1.95.

2. LINEAR THERMAL EXPANSION

With the exception shown in figure 1, all of the expansion-temperature relations appear as smooth curves and the values are given as average coefficients in table 1. Tests made on the α form of the tetralead silicate were unsatisfactory because of the extreme friability of the specimens.

TABLE 1.—*Average coefficients of linear thermal expansion for* PbO, *the compounds in the* $PbO–SiO_2$ *system, and two other mixtures*

Mol ratio $PbO:SiO_2$	Test number	Coefficients [a]			
		Room temperature to 200 C	200 to 300 C	300 to 400 C	400 to 500 C
37:63 Glass	2	8.5	7.9	8.1	[b](495)
1:1 Glass	2	9.2	10.4	9.3	[b](425)
1:1 Crystal	2	7.2	8.8	9.3	9.1
2:1 Glass	2	10.5	13.1	[b] (370)	
2:1 Crystal	2	12.0	13.4	15.2	15.4
3:1 Crystals	2	[c] 10.0			
4:1 Crystal	3	([d])	15.5	13.8	12.5
PbO Crystal	2	25	30	30	28

[a] Coefficients to be multiplied by 10^{-6}.
[b] Beginning of softening, degrees C.
[c] Expansion retarded between 100 and 150 C due to presence of $4PbO.SiO_2$.
[d] Contracts between 137 and 153 C.

3. THE PHASE EQUILIBRIUM DIAGRAM

The phase equilibrium diagram is shown in figure 2.

From the melting point of PbO ($886 \pm 2°$ C) the liquidus drops sharply to approximately 725 C at about 21 mol percent (6.7 wt percent) SiO_2, in which region PbO is the primary phase. At about 725 C the $4PbO.SiO_2$ compound begins to separate out as large crystals of high double refraction (α form). However, when the fused sample is quenched and then held at or below 720 C, a form (designated β) develops which, in turn, undergoes a reversible inversion in the temperature range 120 to 155 C (fig. 1).[11] The results of heating curves, as well as of the quenching tests, are not entirely satisfactory as regards the establishment of the $\alpha \rightleftharpoons \beta$ inversion, but are believed to indicate that the tetralead silicate, on heating, undergoes an inversion at $720 \pm 2°$ C. The liquidus of 20 mol percent silica, which is the composition of the compound $4PbO.SiO_2$, is about 735 C.

From the composition marking the limit of the region in which PbO is the primary phase, to the composition of the $4PbO.SiO_2$–$2PbO.SiO_2$ eutectic at 25 mol percent (8.22 wt percent) SiO_2, the tetralead silicate is the primary phase and the liquidus drops gradually from $725 \pm 2°$ C to $714 \pm 3°$ C, the tetralead silicate-orthosilicate eutectic temperature.

The liquidus then rises to $743 \pm 3°$ C, the melting point of the orthosilicate, and as the content of SiO_2 is increased it drops gradually to $716 \pm 3°$ C at about 40.5 mol percent (15.4 wt percent) SiO_2, which values are the melting point and composition respectively of the orthosilicate-metasilicate eutectic. In this region the orthosilicate is the primary phase.

From the $2PbO.SiO_2$–$PbO.SiO_2$ eutectic the liquidus rises, steeply at first, to $764 \pm 3°$ C, the melting point of the metasilicate. The liquidus then drops, gradually at first, to the metasilicate-silica eutectic temperature ($732 \pm 2°$ C) at approximately 61 mol percent (29.6 wt percent) SiO_2. The metasilicate constitutes the primary phase in this region.

Increasing the silica over the composition of the metasilicate-silica eutectic causes the liquidus to rise very steeply from $732 \pm 3°$ C

[11] Heating curves showed a maximum differential temperature at 138 C while microscopic observations on a heated stage (made by C. P. Saylor of the chemistry division of the National Bureau of Standards) showed crystal movements, caused by volume changes, and increased birefringence beginning at temperatures as low as 100 C and continuing to temperatures as high as 170 C. On cooling, the evidence of a transformation was observable but less clearly defined by either method.

for 61 mol percent SiO_2 to $880 \pm 5°$ C for 62.5 mol percent and approximately 930 C for 66 mol percent SiO_2. Compositions higher in SiO_2 were not investigated, it being considered sufficient to have established that SiO_2 becomes the primary phase for compositions containing more than 61 mol percent SiO_2 and that the liquidus must therefore rise from the eutectic temperature at that composition to the melting point of SiO_2 at 1713 C.[12]

V. DISCUSSION

Values for critical temperatures determined from heating curves obtained by the differential thermocouple method were consistently higher than values obtained by the method of quenching. This variation ranged from a maximum of 8° C for the melting point of PbO to a minimum of 4° C for the melting point of the tetrasilicate-orthosilicate eutectic composition. The indicated values (fig. 2) for the melting temperatures of compounds and eutectics include the values obtained by each method but, in drawing the diagram, preference was given the values obtained by the quenching method with the exception of values for the liquidus temperatures of compositions in which PbO is the primary phase.

The establishment of the melting point of PbO by examination of quenched samples was difficult because of practically instantaneous crystallization; specimens of litharge heated to 875 C and quenched appeared unaffected, while those heated to 880 C and quenched had crystallized as large plates. The results of the differential thermocouple method indicated 886 C as the melting point, which value is in agreement with the value reported by V. A. Kroll [13] and by Krakau and Vachrameev.[14] Many other values have been reported from time to time ranging from 830 to 906 C.[15] Neither the linear thermal expansion curve from room temperature to 500 C nor the heating curve above 500 C indicated a temperature for the massicot-litharge inversion.

The formation of the compound $4PbO.SiO_2$ has not heretofore been mentioned in the literature; several investigators, however, attempted to identify the compound $3PbO.SiO_2$ which would differ from the former, in composition, by only 1.92 wt percent SiO_2. Krakau and Vachrameev [16] describe crystals which they conclude to be $3PbO.SiO_2$, but offer no direct supporting data. Their description of these crystals coincides with the description, given in this paper, of the compound $4PbO.SiO_2$. Cooper Kraus and Klein [17] and Hilpert and Nacken [18] also were unable to prove the formation of trilead silicate. In this investigation mixtures containing 20 mol percent SiO_2 were found to crystallize as a single phase which, on heating to temperatures between approximately 725 and 735 C, formed PbO and glass.

Krakau and Vachrameev [19] describe two biaxial crystal forms of the composition $2PbO.SiO_2$, namely, prismatic and platy, the former having positive elongation and a small optic axial angle and the latter characterized by relatively low interference colors, irregular fracture,

[12] J. W. Greig, Amer. J. Sci. [5] 13, 1 (1927).
[13] Ztschr. Anorg. Chem. 78, 95 (1912).
[14] See footnote 1, p. 237.
[15] J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry; Longmans, Green & Co., New York, N.Y.
[16] See footnote 1, p. 237
[17, 18] See footnote 1, p. 237.
[19] See footnote 1, p. 237.

and an optic axial angle of 50°. They obtained, also, by heating curves, indications of a transformation at 620 C. In this investigation no evidence of a polymorphic change at 620 C was obtained by

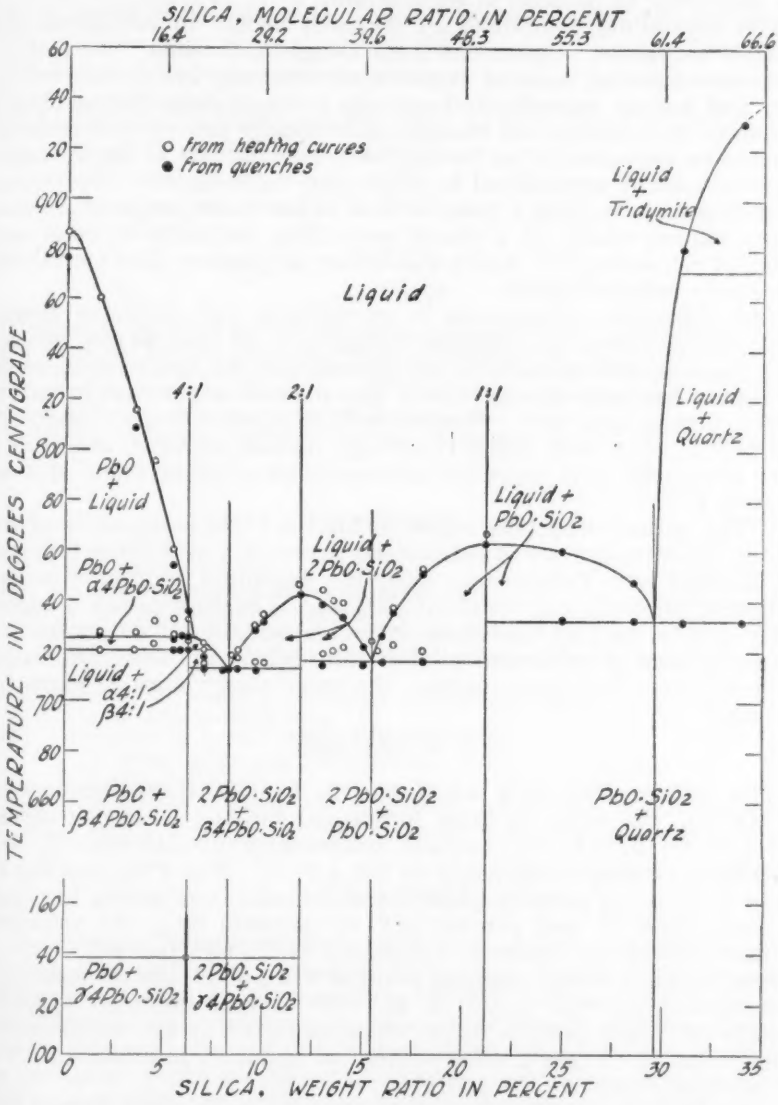

FIGURE 2.—*Phase equilibrium diagram for the system* PbO–SiO$_2$.

means of heating curves, by linear thermal expansion determinations, or by quenching.

Heating curves of mixtures containing from 35 to 40 mol percent SiO$_2$, which had been permitted to crystallize for 3 days or more at temperatures favoring crystal growth, showed two breaks correspond-

ing to the melting temperature of the eutectic mixture and to the liquidus. Conflicting results, such as the three breaks reported by Cooper Kraus and Klein,[20] were obtained when crystallization was not permitted to proceed to equilibrium.

The crystalline compound $3PbO.2SiO_2$ occurs in nature as the mineral barysilite. Specimens from Langban, Sweden [21] were clear, transparent plates, uniaxial negative, of extremely low double refraction and having an estimated average index of refraction of 2.04.[22] Attempts to produce this compound artificially proved unsuccessful. Specimens quenched after having been held at 705 C for 20 hours were completely crystallized to ortho- and meta-silicate. Specimens quenched after holding 3 hours or less at the same temperature consisted almost wholly of a phase resembling barysilite in color and index of refraction, but which was either all glass or glass containing extremely minute crystals.

The difficulties encountered in crystallizing and obtaining significant heating curves for mixtures containing more than 40 mol percent SiO_2 made it impracticable to use this method for mixtures higher in SiO_2 than the metasilicate ratio. The metasilicate occurs in nature as the mineral alamosite. Specimens from Alamos, Sonora, Mexico,[23] are yellow, of no well defined cleavage, biaxial negative, and have a very large optic axial angle and average index of refraction of approximately 1.96.[24]

The optical properties reported for the three compounds of the system investigated are in substantial agreement with those reported by Krakau and Vachrameev with the exception of the refractive indices of the ortho and tetralead silicates. The discrepancy is apparently due to the fact that these investigators did not determine the actual indices of refraction of the sulfur-selenium immersion media used by them but used, instead, the calculated values as given by Larsen.[25]

VI. SUMMARY

The system PbO–SiO_2 was found to contain three compounds: $4PbO.SiO_2$, occurring in three forms and melting incongruently at $725 \pm 1°$ C; $2PbO.SiO_2$, melting congruently at $743 \pm 3°$ C; and $PbO.SiO_2$, melting congruently at $764 \pm 3°$ C. The PbO, melting at $886 \pm 2°$ C, is the primary phase for all mixtures containing less than approximately 21 mol percent (6.7 wt percent) SiO_2; the tetralead silicate-orthosilicate eutectic was found at 25 mol percent (8.22 wt percent) SiO_2, having a melting point of $714 \pm 3°$ C; the orthosilicate-metasilicate eutectic melts at $716 \pm 3°$ C and contains approximately 40.5 mol percent (15.4 wt percent) SiO_2; the metasilicate-silica eutectic, having a silica content of about 61 mol percent (29.6 wt percent), melts at $732 \pm 3°$ C.

WASHINGTON, June 11, 1934.

[20] See footnote 1, p. 237.
[21] U.S. National Museum no. 95103.
[22] Larsen (see footnote 10, p. 239) gives, for the indices of refraction: $\epsilon = 2.05$; $\omega = 2.07$.
[23] U.S. National Museum no. 92990.
[24] Larsen (see footnote 10, p. 239) gives, for the indices of refraction: $\alpha = 1.947$; $\beta = 1.961$; $\gamma = 1.968$.
[25] See footnote 10, p. 239.

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COLLOIDAL NATURE AND RELATED PROPERTIES OF CLAYS

By W. W. Meyer

ABSTRACT

A theory is presented on the colloidal nature and related properties of clays, based upon the findings of certain soil scientists and the existing knowledge of the phenomena of coagulation, deflocculation, plasticity, drying shrinkage, and dry transverse strength. It is thought that this paper will allay some of the present confusion of ideas concerning the subject of clay colloids by adaptation of this theory to furnish a more satisfactory explanation of the above phenomena.

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I. INTRODUCTION

A review of the ceramic literature yields a confusion of ideas concerning clay colloids. Ceramists have thus far advanced no complete theory capable of explaining clearly the mechanism of the phenomena of deflocculation, coagulation, plasticity, drying shrinkage and dry strength of clays and the variation of these properties caused by variations in the treatment of a given clay. The general impression gained from the early literature is that clays are composed of extremely small, negatively charged, active colloid particles covering the surfaces of larger inert particles. This thin coating of colloidal particles is said to account, in varying degrees, for the above phenomena, but the explanation of the chemistry or physics involved seems always to be hazy. For example, at what size does a particle cease to be an active colloid and become inert and why has the larger particle no charge if the smaller one of like composition has a negative

charge? The variation in ideas concerning this general subject can be found in comparatively recent papers.[1][2][3][4][5][6] Vickers mentioned the subject of base exchange; Hissink gave the manner in which exchangeable bases occur on the clay particle. Marshall went into the subject in more detail and also pointed out the fact that colloidality of clays increases with a decrease in particle size, thus apparently not considering the colloids as a separate and distinct group of particles, as most writers had done previously.

Theories capable of explaining quite satisfactorily the behavior of soil colloids have been advanced by Mattson.[7] Certain of these theories, if properly interpreted, can be used to explain the phenomena exhibited by ceramic clays and clay colloids. After digesting the voluminous and detailed works of Mattson and the writings of others, the author of this paper presents, with some modifications or added interpretations where these are justified or necessary, such of the theories as are needed to account for the behavior of ceramic clays and clay colloids. The adaptation of the theories to the known facts is attempted in the latter part of this paper.

In order to simplify the explanations of various reactions it will be necessary to assume, in some cases, ideal conditions which may never quite exist, as for example, equilibrium between the clay and the weathering solution or the suspending medium.

II. TERMS AND DEFINITIONS

It is thought that the following terms and definitions, most of which are well known in the field of soil science, might be of assistance to those readers who are unfamiliar with this field. The symbols in brackets at the end of each definition correspond with the symbols in figure 1.

Clay particle.—A core composed of one or more molecules, and carrying on its surface basic and acidic groups or atoms, or positive and negative ionic charges, or both. [(1) plus (2)].

Micellar ion atmosphere.—An atmosphere of adsorbed and unadsorbed ions surrounding the particle. [(3)].

Micelle.—The clay particle, its ionic atmosphere and imbibed water (see section VI). [(1) plus (2) plus (3)].

Intermicellar ions.—Ions in solution outside of the micellar atmosphere [(−) and (+) in zone (4)].

Colloid complex.—The active particle surface together with its micellar ion atmosphere and imbibed water [(2) plus (3)].

Acidic constituents.—Those integral components of the particle which have a negative ionic charge when ionized (the acid radicals of weak acids) [A].

Amphoteric constituents.—Those integral components of the particle which ordinarily have a positive ionic charge when ionized, but can have a negative charge [B].

Ionic charges (on the particle surface).—Positive and negative charges at the particle surface resulting from ionization of acidic and basic residues or their reaction products [+ and − in zone (2)].

[1] McDowell, J. Am. Ceram. Soc., [4]10, 225(1927).
[2] Vickers, Ceram. Soc. Trans., 28,91 and 124(1929).
[3] Hall, Jour. Am. Ceram. Soc., [10]13,751(1930).
[4] Marshall, Ceram. Soc. Trans., 30,81(1931).
[5] Hissink, Trans. Faraday Soc., 20,551(1924-25).
[6] Ashley, Techn. Pap. BS.23, 33(1911).
[7] Soil Science, 30,459(1930); 31,311(1931); 32,343(1931); 33,301(1932); 34,209 and 459(1932).

Adsorbed atoms or groups.—Basic and acidic atoms or groups held on the surface of the clay particle by valence bonds ○ in zone (2)].

Adsorbed ions.—Those ions held in the atmosphere about the clay particle by opposite ionic charges on the particle surface [⊕ and ⊖ in zone (3)].

Unadsorbed micellar ions.—Ions in the micellar atmosphere not held by opposite ionic charges on the particle surface (see section VI). [(+) and (−) in zone (3)].

Acidic residue.—That portion of the acid remaining unneutralized after reaction (partial combination) of a weak acid with a weak base, e.g., compare partial neutralization:

$3H_2SiO_3+2Al(OH)_3 \rightarrow H_3(3SiO_3 \equiv 2Al)(OH)_3+3H_2O$, with complete neutralization:

$$3H_2SiO_3+2Al(OH)_3 \rightarrow (3SiO_3 \equiv\!\equiv 2Al)+6H_2O.$$

Basic residue.—That portion of the base remaining unneutralized after reaction (partial combination) of a weak acid with a weak base.

Acidoid.—A colloid which reacts as an acid, e.g., colloidal silicic acid.

Ampholytoid.—A colloid which can act either as an acid or as a base depending upon its environment, e.g., colloidal aluminum and ferric hydroxides. (It is said that there are no basoids.)

Silica:Sesquioxide ratio.—A term commonly used to express the ratio of acidic to amphoteric constituents or the acidoid to ampholytoid ratio of soil and clay colloids, because silicic acid and aluminum and ferric hydroxides are the chief reactants in the formation of these colloids. [Numerically this ratio is equal to 2A/B].

III. THE CLAY PARTICLE AND THE COLLOIDAL COMPLEX

1. FORMATION OF CLAY PARTICLES

From Mattson's work [8] it is apparent that completely weathered clays are made up of particles of various sizes, formed by the reaction (partial or complete combination) of weak acids, e.g., silicic acid, and weak bases, e.g., aluminum and ferric hydroxides, derived from the parent rock. The particles formed will be crystalline or amorphous, depending upon existing conditions. In either case there will be acidic and basic residues at the particle surfaces (fig. 1).

It can be seen from the illustration that this surface condition exists regardless of the particle size and therefore any property caused by it would be more likely a function of specific surface than of the percentage of material below a given particle size.

According to Mattson the acidic and basic residues of the particle are free to react, under favorable conditions, with other constituents of the clay or leaching solution. That is, the particle can grow through displacement of the hydroxyl group and the hydrogen by more of the acids and bases already present, or by other anions and cations in the weathering solution, which, upon uniting with the particle, will hinder or arrest further growth if they do not fit into its internal structure. For this reason the presence in the weathering solution of material foreign to the pure end product of the weathering process will retard the formation of the end product. The anions or

[8] See footnote 7, p. 246.

cations reacting with the basic or acidic residues of the particle may be monovalent, e.g., Cl^- or Na^+, polyvalent, e.g., PO_4^{---} or Ca^{++}, or more complex ions such as $\left(-Al\langle^{OH}_{OH}\right)^+$ or $(H-SiO_3-)^-$. A polyvalent ion may unite with the clay particle by one bond and then with one or more ions of opposite charge, depending upon the number of remaining valences (fig. 2). In this manner, a layer of varying degree of heterogeneity, depending upon the prevailing conditions, might be built up on the surface of the clay particle.

An ion of sufficient concentration might even replace some of the acidic or basic constituents of the particle. However, such ionic concentrations are probably not common in normal weathering or

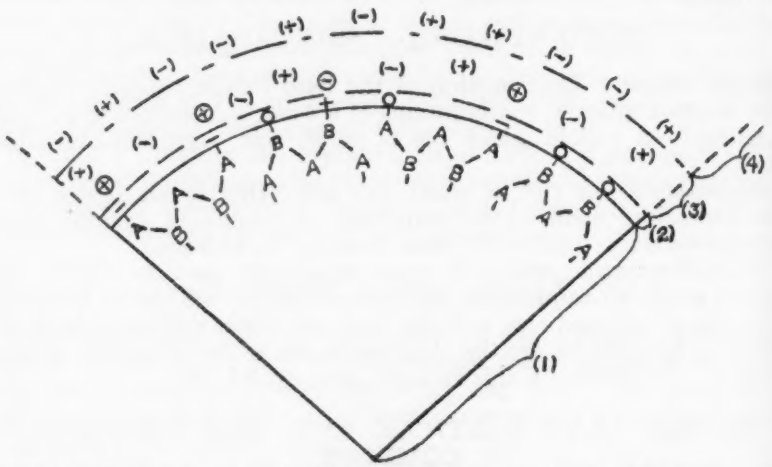

FIGURE 1.—*Portion of a hypothetical clay micelle, showing the component parts.*

[See text, p. 247.]

ceramic processes. It is believed that by far most of the reactions of the clay, which are dependent upon the acidic and basic residues, take place at the particle surfaces and hence are a function of the specific surface of the clay.

2. COLLOID COMPLEX—THE SOURCE OF COLLOIDALITY OF CLAYS

The outside layer of the clay particle together with its adsorbed ions is called the colloidal complex, since nearly all of the reactions which give clays colloidal properties take place here. The upper limit of colloidal particle size has been accepted by most workers in colloid chemistry as 0.1 micron in diameter. However, English china clays exhibit colloidal properties to some degree and yet Marshall[9] found that they contained practically no particles less than 0.1 micron in diameter. The soil chemists have accepted 2 microns as the diameter of the largest particles exhibiting colloidal properties.[10] The lack of a definite upper size limit of colloidal clay particles may be explained if it is assumed that the whole particle is not necessarily

[9] See footnote 4, p. 246.
[10] U.S. Dept. of Agri., Tech. Bull. 170.

colloidally active, but that it has a stable core with an active surface. It can readily be seen that a clay composed of two-micron particles with a very active surface complex might exhibit colloidal properties to a greater extent than a clay composed of one-micron particles with a much less active surface complex. The exhibition of colloidal properties would, therefore, depend not only upon particle size but also upon the activity of the surface layer.

IV. RELATION OF pH OF WEATHERING SOLUTION TO COMPOSITION AND ISOELECTRIC pH

It was pointed out that, under favorable conditions, the clay particle could enter into various reactions. These conditions depend upon the concentrations of the various ions present. Even at the isoelectric point, in which condition a clay is most stable, the acidic and basic residues are ionized to some extent. By definition[11] the positive charges on the particles equal the negative charges at the isoelectric point (or $H^+ = OH^-$), regardless of the ratio of acidic to basic residue. This condition might be represented by figure 3.

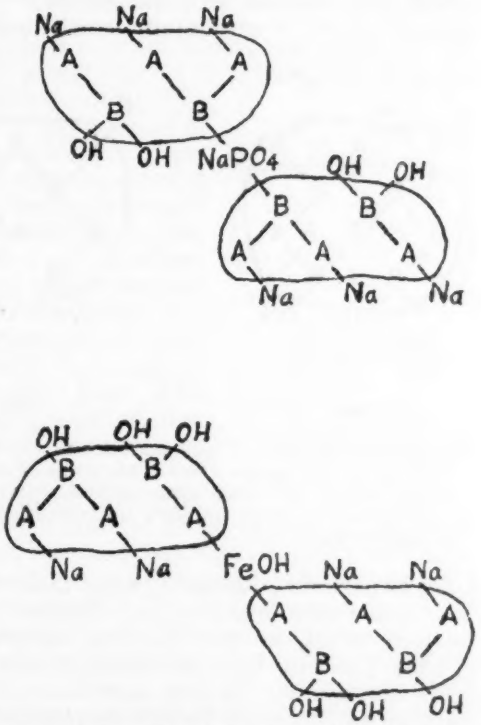

FIGURE 2.—*Mutual bonding of particles by polyvalent ions.*

It can be seen that particle (a) would be isoelectric at a lower pH value than would particle (b) because the former would require more hydrogen ions in solution to suppress the ionization of the hydrogen atoms on the particle. Thus, the higher the ratio of the acidic residue to the basic residue of the particle, the lower will be the isoelectric pH.[12]

Since clay is most stable at its isoelectric point, it will tend to weather to that composition which is in the isoelectric condition at the pH value of the weathering solution. This has been found to be the case in nature.[13] In cold, damp climates, where the pH values of the weathering solutions are low, the product has a higher ratio of acidic to amphoteric constituents (silica to sesquioxides) than in moist warm climates, where the pH values of the weathering solutions are higher. To explain this, suppose particle (a), figure 3, is isoelectric at pH 3. If it is leached by a solution having a pH value

[11] Soil Sci., 34, 209 (1932). [12] See footnote 11. [13] See footnote 11.

of 5, the ionization of the hydroxyl groups will be suppressed and of the hydrogen atoms will be encouraged. Now, if the solution contains such ions as $\left(-\mathrm{Al}\langle\begin{matrix}\mathrm{OH}\\\mathrm{OH}\end{matrix}\right)^{+}$, they will displace hydrogen ions and combine with the particle. This change will decrease the ratio of acidic to amphoteric constituents (acidoid to ampholytoid ratio), thus lowering the ratio of acidic to basic residue, until the hydrogen and hydroxyl ions dissociated from the clay particle are again equal in number. Suppose particle (b), figure 3, is isoelectric at pH 5. If it is leached by a solution containing such ions as $(\mathrm{H}-\mathrm{SiO_3}-)^{-}$ and having a pH value of 3, the ionization of the residual hydrogen atoms will be suppressed and of the hydroxyl groups will be encouraged, resulting in the displacement of the latter by the above complex ion which will combine with the particle. This change will increase the ratio of acidic to amphoteric constituents, thus lowering the ratio of acidic to basic residue until the hydrogen and hydroxyl ions dissociated from the particle are again equal in number.

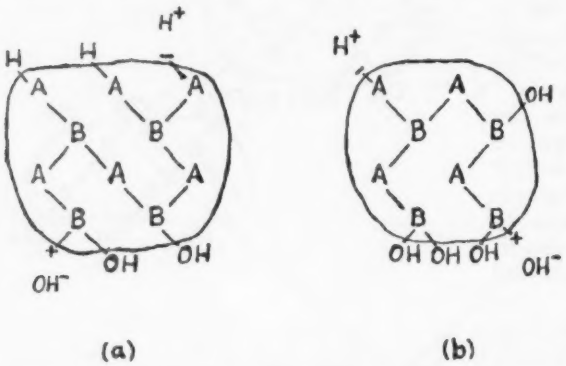

FIGURE 3.—*Portions of clay particles in the isoelectric condition, showing the effect of the ratio of acidic* (A) *to amphoteric* (B) *constituents upon the ratio of acidic to basic residues at the surface;* (a) *beidellite ratio;* (b) *kaolinite ratio.*

It is conceivable that colloidal clay particles can be composed of any number of molecules of any size, the atoms and molecules being held together by various types of valences. There may be almost any imaginable ratio of acidic to amphoteric constituents within these molecules or particles, depending upon their environment during formation. The ratios with which we are familiar persist because on combining in these ratios, weather-resistant minerals are formed.

Clay particles hold hydroxyl groups more strongly than they do hydrogen atoms. If this were not so, a clay of the composition of particle (a), figure 3 (which corresponds to that of the mineral beidellite), would have an isoelectric pH of 7, whereas actually its isoelectric point is at a much lower pH value.

V. ULTIMATE pH, EXCHANGE NEUTRALITY AND EXCHANGE CAPACITY

In figure 3 the clay particles were represented as completely unsaturated, i.e., free from any adsorbed ions, atoms or groups other than hydrogen and hydroxyl. This condition is obtainable by leaching the clay sample with distilled water to remove soluble salts and then electrodialyzing it. In electrodialysis a direct current is passed from an anode through the clay suspension, which is held by a porous membrane, to a cathode. Hydrogen ions, produced by the electric current, are carried through the clay in sufficient concentration to dis-

place the adsorbed bases, which are carried through the porous membrane to the cathode by the current and removed by constant flow of water. Furthermore, figure 3 shows the particles to be in the isoelectric condition. To arrive at this condition it is necessary to add to the suspension of electrodialyzed clay sufficient reagent to bring the water to the isoelectric pH of the clay. The pH value of the suspension of the electrodialyzed sample is called the ultimate pH, which lies between pH 7 and the isoelectric pH.[14] It varies with the concentration of the suspension, approaching the isoelectric pH as the concentration increases, and is conveniently determined in a suspension of one gram of material in 25 ml of distilled water.

The pH of exchange neutrality is that point at which the clay particles adsorb equal numbers of the cations and anions of a neutral salt,[15] and it differs for different salts. This condition is illustrated in figure 4.

The ultimate pH can be determined by adding one gram of the electrodialyzed, dried and pulverized clay to 25 ml of distilled water and determining the pH the following day. The pH of the original clay could be determined in the same manner. To determine the pH of exchange neutrality and the exchange capacity of a clay at any pH,[16] make up stock solutions of 0.1 normal sodium chloride, containing 0.0, 0.05, 0.1, 0.2, and 0.3 milliequivalent of added sodium hydroxide and 0.05, 0.1, and 0.2 milliequivalent of added hydrogen chloride, respectively, per 25 ml of solution. First determine the pH value of each of the solutions and plot them against the milliequivalents of added acid or base. This will give the curve for the neutral salt solution (fig. 5). Now leach and electrodialyze 10 grams of clay (preferably using the Salgado and Chapman cell).[17] Dry on a water bath and pulverize the electrodialyzed clay and add 1 gram to 25 ml of each of the stock solutions. Shake one-half hour, let stand over night and determine the pH of each. Plot the curve for pH versus milliequivalents of added acid or base. The point at which the curve for the clay suspension intersects that for the neutral salt solution represents the pH of exchange neutrality. At any given pH, the horizontal distance between the two curves represents the exchange capacity of the clay in equilibrium with the neutral salt (sodium chloride) for chlorine or for sodium, as the case may be.

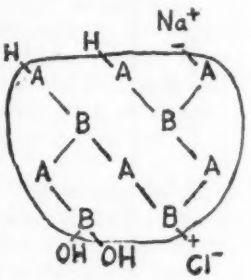

FIGURE 4.—*Portion of a clay particle in the condition of exchange neutrality.*

The increase in base exchange capacity of a given clay with an increase in pH value must have an upper limit for the same reason that there is a lower limit in pH value at which maximum anionic adsorption occurs, i.e., a change occurs in the nature of the clay particles.

If the combination of the clay with the cations of the salt has the same stability as that with the anions of the salt, the pH of exchange neutrality will be the same as the isoelectric pH.[18] This is practically true for sodium chloride.[18] If sodium sulphate were used the sulphate, forming a more stable compound with the clay (being more strongly adsorbed), would displace more hydroxyl ions than the num-

[14] See footnote 11, p. 249.
[15] See footnote 11, p. 249.
[16] This procedure varies slightly from that of Mattson; Soil Science, 34,459(1932).
[17] Soil Science, 32,199(1931).
[18] See footnote 11, p. 249.

ber of hydrogen ions displaced by the sodium, thus giving the suspension, at exchange neutrality, a pH higher than the isoelectric pH.

The degree of dissociation of a salt formed by union of ions with a given clay particle depends upon the ions entering into this union. The decreasing order of this degree of dissociation for some cations and some anions seems to be $Na>K>Ca>H>Fe>Al$ and $Cl>SO_4>SiO_3>PO_4>OH$.[19] The Hofmeister series, which takes into account both valence and the nature of the ion, seems to obtain.[20] The

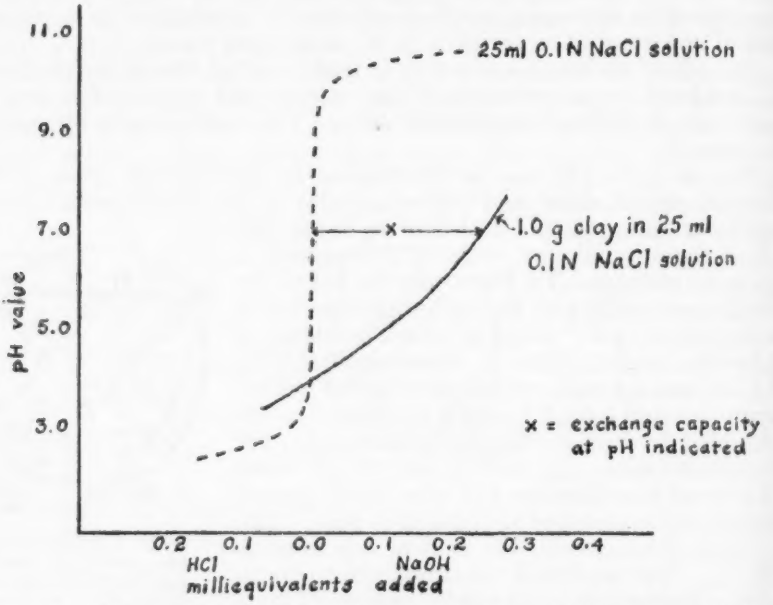

FIGURE 5.—*Determination of* pH *of exchange neutrality and exchange capacity (from Mattson with slight modification).*

order of the stability of the compounds formed by these ions with clay particles is the reverse of the above.

It has been shown [21] that, with a given sesquioxide composition, an increase in the silica to sesquioxide ratio of the particle causes a decrease in the pH of exchange neutrality (and for that matter, also of the isoelectric pH and the ultimate pH, since they are not greatly different). Mattson [22] has found that a substitution of iron for aluminum in the sesquioxide lowers the pH of exchange neutrality on account of the less nearly complete combination between iron and the silicate than between aluminum and the silicate, thus making available more acid residue and hence increased absorption capacity for cations (or base exchange capacity). Incidentally, the adsorption capacity for anions is increased a like amount by this less nearly complete combination, but the great stability of the hydroxyl-clay complex prevents appreciable displacement of the hydroxyl ions until a very low pH is reached. Displacement of silicate by humate or phosphate has an effect on exchange neutrality and exchange capacity similar to that of replacing aluminum with iron.[23] The effect of the

[19] Soil Science, 34,459(1932).
[20] Soil Sci., 33,301(1932).
[21] See footnote 19, p. 252.
[22] See footnote 19, p. 252.
[23] See footnote 19, p. 252.

latter replacement might be represented by a comparison of $H_3(3SiO_3 \equiv 2Al)(OH)_3$ with $H_4(3SiO_3 = 2Fe)(OH)_4$.

It should be borne in mind that the presence of clay minerals, which contain as integral parts of their structure alkali or alkali earth atoms, will, if Marshall [24] is correct in his statement that these atoms are exchangeable, modify the relation between the exchange capacity at a given pH and the acidoid to ampholytoid ratio of the particle surfaces. Internal base exchange will also affect the relation between base exchange capacity and those properties which depend upon the activity of the particle surfaces; for the occurrence of internal base exchange would result in a less active surface than that indicated by the relation between exchange capacity and specific surface.

VI. WATER OF OSMOTIC IMBIBITION [25]

Before discussing imbibed water it might be well to mention briefly the three other types of water common to clays. They are (1) combined water, held in the form of hydrous oxides; (2) hygroscopic water, held on the particle surfaces by molecular attraction; (3) capillary water, held in fine capillaries and interstices by surface tension. The hygroscopic water is very firmly held in a layer which has been variously measured as 2.5 to 5.0 millimicrons in thickness.[26] This layer is practically rigid because of the force with which it is held. It is evidenced by heat of wetting and by compression of the solid particles.

Up to this point exchange reactions have been represented as direct combinations of ions with clay particles by the conventional valence bonds. Now it is convenient and logical to make use of the double layer theory. The surface of the clay particle is covered, more or less thickly, depending upon its composition and the pH of its suspension, with a layer of positive and negative ionic charges. The algebraic sum of these charges is positive when the pH of the surrounding solution is below the pH of exchange neutrality (because of the high concentration of H^+ ions which neutralize the negative ionic charges), making possible adsorption or attraction of anions,[27] and negative when the pH of the solution is above this pH, making possible adsorption or attraction of cations. The latter condition is the one most common to ceramic clays and processes. Outside this layer is the second layer composed of an atmosphere of adsorbed diffusible ions, bringing the micelle, as the whole is called, into equilibrium with the surrounding or intermicellar solution, according to the Donnan equilibrium equation.[28]

$$x^2 = y(y + z)$$

where:

x = ionic concentration of the cations and of the anions in the intermicellar solution (total $= 2x$).

y = ionic concentration of the cations and of the anions in the micellar solution (total $= 2y$).

z = ionic concentration of the adsorbed ions, i.e., the ions whose charges are attracted by the clay particle.

[24] See footnote 4, p. 246.
[25] See footnote 20, p. 252.
[26] See footnote 20, p. 252.
[27] As shown in Mattson's work, see footnote 19, p. 252.
[28] See footnote 20, p. 252.

This condition of equilibrium might be represented by figure 6. The osmotically imbibed water is held by this ion atmosphere surrounding the clay particle in a layer of varying thickness and viscosity depending upon the density and thickness of the atmosphere. It is self-evident that:

$$(2y+z)-2x=e=\text{excess micellar ions}$$

Therefore, since the osmotic pressure in the micelle is proportional to the excess (e) [29] of ions present, it can be seen that a decrease of "z" caused by substitution of an ion lower in the Hofmeister series (calcium) for one higher in the series (sodium) or an increase in "x" (with "z" constant) caused by addition of free electrolyte to the intermicellar solution, would reduce the amount of imbibed water per unit surface of the particle. This relation has been proved by experiment.[30]

The base exchange capacity of a clay, at any given pH, indicates its capacity for osmotic imbibition of water when saturated with a given ion at that pH. The imbibition is evidenced by swelling of the

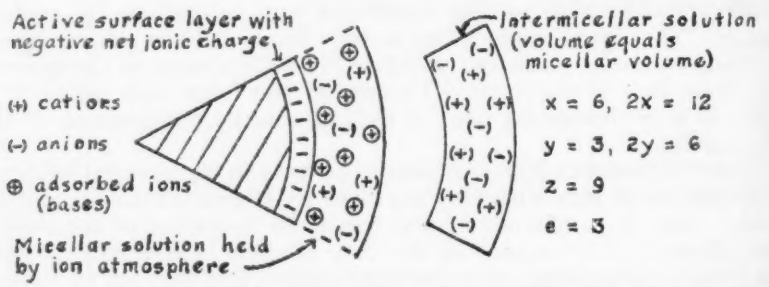
Active surface layer with negative net ionic charge
(+) cations
(-) anions
⊕ adsorbed ions (bases)
Micellar solution held by ion atmosphere
Intermicellar solution (volume equals micellar volume)
x = 6, 2x = 12
y = 3, 2y = 6
z = 9
e = 3

FIGURE 6.—*Donnan equilibrium condition (from Mattson with slight modification).*

clay mass. Tests on fine fractions of various soils and clays have shown that a very active particle surface may cause imbibition of a layer of water up to 23 to 45 millimicrons in thickness when treated with an ion such as sodium. This thickness was calculated by the author from Mattson's data on average particle size and imbibitional swelling.[31] To illustrate the effect of particle size let us assume three spherical particles, 10 microns, 1 micron and 0.1 micron in diameter, respectively, each imbibing a layer of water 25 millimicrons in thickness. The volume of water imbibed by the 10-micron particle will be 1.5 percent, by the 1-micron particle 15.8 percent, and by the 0.1-micron particle 238 percent of the original volume of the particle. It is evident that, other conditions being constant, the colloidality of a clay (if we assume imbibition to be a distinctly colloidal property) increases greatly as the particle size decreases or the specific surface increases.

Mattson found [32] that the imbibed water in a clay can be removed by application of pressure, the volume removed being proportional to the cube root of the pressure applied. He states that this relation is caused by the increase in osmotic pressure as the micellar ion concentration increases on approaching the particle surface.

[29] See footnote 20, p. 252.
[30] See footnote 20, p. 252.
[31] See footnote 20, p. 252.
[32] See footnote 20, p. 252.

VII. APPLICATION TO CERTAIN CERAMIC PHENOMENA

1. COAGULATION AND DEFLOCCULATION

In practically all literature on the subject [33] [34] deflocculation of clay suspensions has been attributed to the repulsion of particles of like charge, while coagulation is said to be due to the neutralization of the charges on the particles. The negative charges on the clay particles are assumed to be the result of selective adsorption of the hydroxyl ion.

According to the theory presented here it is true that the particle proper has a negative net ionic charge increasing from just above the isoelectric pH, at which the net charge of the particle proper is zero, to a maximum at the pH of maximum deflocculation. This negative ionic charge is due to the increased dissociation of adsorbed basic atoms or groups and the decreased dissociation of adsorbed acidic atoms or groups from the clay particle as the pH of the suspending medium is increased. Now, if at the same time the pH is increased a cation high in the Hofmeister series is added to the suspension in sufficient concentration to replace the adsorbed ions lower in the series, the number of ionic charges on the clay particle proper will be further increased. However, for every negative ionic charge on the particle there is a positive ionic charge on a cation in the micellar atmosphere and even though they may not neutralize each other completely individually, the net negative charge of the particle will always be equal to the net positive charge of its atmosphere under equilibrium conditions. It is reasonable to believe that two such micelles approaching each other in suspension would be repelled by the like net ionic charges of their particles and of their atmospheres but would be attracted an equal amount by the unlike net ionic charges of the particle of each and the atmosphere of the other.

The motion of the particle in an electric field is caused by upsetting the equilibrium or changing the potential between the particle surface and its ion atmosphere, the cations being attracted by the cathode and the negative particle by the anode. At the isoelectric pH there is zero potential between the particle and its atmosphere and hence an electric field produces no motion of the particle.

In the coagulated condition the layer of imbibed water is thin and hence the clay particles are close enough together to attract each other molecularly. Also, the presence of polyvalent ions would make it possible for one ion to neutralize opposite ionic charges on more than one particle, thus holding the particles together. This phenomenon has been investigated by Marshall,[35] who advances the theory of orientated coagulation of clay particles by polyvalent ions.

In the deflocculated condition the clay particles are surrounded by imbibed water layers of sufficient thickness to prevent their molecular interattraction to any extent. This theory explains the greater ease of deflocculating such clays as ball clays, which imbibe large amounts of water, as compared to china clays and kaolins, which have less active particle surfaces. This theory will also explain many of the differences in actions of the various deflocculating agents. The monovalent deflocculating ion minimizes coagulation because it

[33] See footnote 1, p. 246.
[34] See footnote 3, p. 246.
[35] See footnote 4, p. 246.

cannot ordinarily act as a bond between particles. Sodium hydroxide increases the pH of a clay suspension more than does sodium silicate, if equal amounts of sodium are added in both cases. The reports made by McDowell [36] concerning pH values of clay slips in the condition of maximum deflocculation are supporting evidence. The more potent deflocculating action of sodium silicate as compared to sodium hydroxide may be explained by the fact that the silicate ions have the effect of increasing the acidoid to ampholytoid ratio of the surface layer of the particle, thus creating more surface activity.

2. PLASTICITY

The plasticity of a clay depends upon the number, thickness, and viscosity of the liquid films surrounding the particles in a given mass and also upon the shape, size distribution, and degree of aggregation of the particles.

The number of films is governed by the number of particles in, or the surface factor of, a given mass of clay, and is in turn a factor in determining the amount of deformation possible without rupture. The thickness of the liquid films regulates the distance between particles, hence the force of molecular attraction between them, and thus influences the force necessary to cause deformation of the mass. The viscosity of the imbibed water films also influences the force necessary to deformation, and is inversely proportional to some function of the film's thickness or the excess micellar ion concentration. Shape, size distribution, and degree of aggregation of the particles will affect the ease with which they will slide or roll over one another (ease of deformation) and also the amount of interstitial space filled by capillary water. The amount of this capillary water will be governed also to some extent by the thickness of the imbibed water films and will in turn influence the consistency of the mass. Possibly the adhesion tension between the clay and the water as discussed by Clark [37] has some influence on plasticity (and deflocculation), but, in view of the work of Mattson previously cited, the conclusion that addition of small quantities of alkalies decreases the thickness of the "absorbed" (imbibed) water films, causing deflocculation, would seem erroneous.

Consider the plasticities of a comparatively coarse-grained kaolin and a fine-grained ball clay. The former will contain fewer and probably thinner imbibed water films, and will imbibe a smaller percentage of the total water necessary to produce plasticity. Due to the greater force between adjacent particles the kaolin will tend to form aggregations which will cause it to retain larger amounts of capillary water and also give the effect of increased particle size. The larger percentage of the more loosely held and less viscous capillary water will result in a softer mass, while the fewer and thinner water films will allow less deformation before rupture takes place.

3. DRYING SHRINKAGE

Drying shrinkage is caused by removal of capillary, imbibed, and usually some hygroscopic water. The first and last depend chiefly upon particle size (or specific surface) and aggregation. The amount

[36] See footnote 1, p. 246.
[37] Trans. Cer. Soc. (Br.), 32, 1(1933).

of water imbibed by the clay depends upon surface area and activity and the concentration and identity of the ions present.

Some of the differences between ball clays and china clays, with respect to the effect of forming pressure on shrinkage during drying and during heat treatment [38] might be explained by variations in the number of adsorbed ions and hence in the imbibed water. The amount of exchangeable bases present will in most cases be some function of the product of the number and thickness of water films separating the particles in a given mass.

4. DRY TRANSVERSE STRENGTH

Dry transverse strength is undoubtedly related to base exchange capacity. This is indicated by the low strengths of china clays and kaolins, which have low exchange capacities,[39] medium strengths of ball kaolins and some (usually light colored) ball clays, which have medium exchange capacities, and high strengths of dark ball clays and some of the common clays [40] high in iron and other impurities, which have high exchange capacities. There are other factors which affect dry transverse strength, but their importance does not outweigh that of the base exchange capacity. Clays have been strengthened by the addition of organic matter which undoubtedly increased the base exchange capacity.

The micellar ions and also any solute which might be left by evaporation of the suspending solution undoubtedly act as a cementing bond between the particles of the dried clay mass. The valence of the adsorbed ion might be an important factor, but this phase of the subject has not yet been investigated.

The fact that some clays have a higher dry transverse strength after addition of some nonplastic material can be attributed to one or both of two reasons: (1) Reduction of the shrinkage, eliminating microscopic drying cracks caused by strain from excessive shrinkage of the clay alone; (2) production of a particle size distribution which results in a smaller percentage area of voids in the cross section of the test specimen.

VIII. DISCUSSION AND SUMMARY

Clay particles are formed by the partial or complete combination of weak acids and weak bases, the ratio of the combination depending upon the pH value of the weathering solution. Basic and acidic residues occur at the particle surfaces, and can dissociate to form an ion (or micellar) atmosphere, leaving ionic charges on the particles. The degree of ionization of these adsorbed atoms and groups is controlled by the concentration of like ions in the intermicellar solution. The ratio of acidic to basic residue of the particle depends upon the composition of the surface layer (which, due to changing conditions, might be different from that of the interior). The nature and number of the micellar ions influence various properties of the clay.

The clay tends to weather to the composition which has an isoelectric pH value equal to the pH value of the weathering solution. For

[38] A. E. R. Westman; J. Am. Cer. Soc., [6]16, 256(1933).
[39] T. A. Klinefelter, W. W. Meyer, and E. J. Vachuska; J. Am. Cer. Soc., [6]16, 269(1933).
[40] T. A. Klinefelter, National Bureau of Standards, Properties of Some Ohio Red-burning Clays (Unpublished).

this reason the more completely a clay is weathered by a given solution, the less fine particles it will contain because it reaches the isoelectric composition. In this condition there is a minimum density of the micellar ion atmosphere, and maximum particle growth resulting from combination of the acidic and basic residues of adjacent particles. A low ratio of acidic to amphoteric constituents (silica to sesquioxide ratio) also corresponds with a low micellar ion density; hence it might be said that the amount of fine particles or the specific surface of a clay, and therefore the "colloidal content", varies inversely with the pH value of the weathering solution and the completeness of weathering. Since weathering is retarded by the presence of impurities we might expect the clay particles in impure clays to be finer grained than those in pure clays.

The colloidal properties of a clay are due to the presence of the ionic atmosphere mentioned above. The maximum size of particles which can exhibit colloidal properties depends upon the activity of their surface layers, which in turn depends upon their compositions. An increase in the ratio of acidic to amphoteric constituents (silica to sesquioxide ratio), or substitution of iron for aluminum or humic acid for silicic acid increases the activity. Osmotic imbibition of water, which depends upon the micellar ion atmosphere, accounts in large measure for the colloidal properties of clays. The base exchange capacity, at a specified pH value, is indicative of a clay's capacity for imbibed water, under given conditions.

Mattson [41] has suggested that soils might be classified chemically as to strength and capacity to react; the strength being indicated by the pH of exchange neutrality and capacity to react by the base exchange capacity at some given pH value. The same could be done for ceramic clays. The determination of these properties, as outlined in this paper, would not only furnish a means of classification, but would yield information which could be applied to the problem of clay beneficiation. There is need of experimental work in applying the theories presented in this paper to the solution of problems involving deflocculation, coagulation, plasticity, drying shrinkage and dry strength of various clays and bodies.

WASHINGTON, June 26, 1934.

[41] See footnote 19, p. 252.

U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP707

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PROLONGED TEMPERING AT 100 C AND AGING AT ROOM TEMPERATURE OF 0.8 PERCENT CARBON STEEL

By G. A. Ellinger and R. L. Sanford

ABSTRACT

Thermomagnetic analysis has been applied to the study of quenched 0.8 percent carbon steel to show the effect of tempering for prolonged periods of time at 100 C and also the effect of aging at room temperature for considerably longer periods. Some specimens were also cooled in liquid air, tempered, and aged. The changes taking place in magnetization are interpreted as constitutional changes taking place in the steel.

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I. INTRODUCTION

In a previous paper [1] there were pointed out some of the advantages and possibilities of thermomagnetic analysis as a method of studying constitutional changes occurring during the tempering of quenched steel. It was possible by this method to follow the progress of the transformations while they were occurring, and some new evidence as to their nature was obtained. The method has been used in the present investigation to study the aging at room temperature of quenched high carbon steel and the effect of prolonged heating at 100 C.

II. MATERIAL AND METHODS

Cylindrical specimens 10 centimeters in length and 5 millimeters in diameter were prepared from basic open-hearth steel of the following composition:

	Percent
Carbon	0.78
Manganese	.56
Phosphorus	.020
Sulphur	.031
Silicon	.11
Chromium	.06
Nickel	.05
Copper	.06

[1] G. A. Ellinger, Thermomagnetic investigation of tempering of quenched 0.75 percent carbon steel, B.S.J. Research, 7, 441(1931); R.P.350; also R. L. Sanford and G. A. Ellinger, Thermomagnetic phenomena in steel, Trans., A.S.S.T., 20, 263(1932).

After normalizing, the specimens were heated in a lead bath maintained at a temperature of 825 C and then quenched in water at 20 C. In order to obtain uniform action during quenching, four specimens were heated and quenched together in a small jig, so designed as to allow free circulation of water around each specimen. After quenching, some of the specimens were immersed in liquid air for a period of 2½ hours. Details of the treatment of each specimen are given in table 1.

TABLE 1.—*Treatment of specimens after quenching from 825 C into water at 20 C*

Specimen	Treatment	Specimen	Treatment
1	As quenched.	8	Tempered 1,500 hours at 100 C, and aged 2 years at room temperature (approximate range 0 to 35 C).
2	Tempered 168 hours at 100 C.	9	Aged 2 years at room temperature.
3	Tempered 360 hours at 100 C.	10	Cooled 2½ hours in liquid air (−190 C).
4	Tempered 750 hours at 100 C.	11	Cooled 2½ hours in liquid air, tempered 1,500 hours at 100 C, and aged 2 years at room temperature.
5	Tempered 1,500 hours at 100 C.		
6	As quenched.		
7	Tempered 1,500 hours at 100 C.		

As an aid in conciseness and brevity specimens held 1,500 hours at 100 C are designated as "tempered" and those kept at room temperature (an approximate extreme range of 0 to 35 C) for 2 years as "aged."

In addition to the thermomagnetic analysis which was carried out with a slightly modified form of the apparatus previously described,[2] the microstructure was examined and the hardness was determined on auxiliary specimens, notched before heat treatment so that small pieces could be broken off when desired during the course of the treatment. The hardness was determined with a Vickers hardness tester.

III. OBSERVATIONS AND RESULTS

In carrying out the thermomagnetic analysis the specimens were subjected to a constant applied magnetizing force of 277 oersteds. The dimensional ratio of the specimen was such as to bring the magnetization always into the third stage. The uncertainties usually encountered when the magnetization is in the unstable second stage, represented by the steep part of the B–H curve were thus avoided.

Two methods of procedure were used. In the first method the specimen was heated at a uniform rate of approximately 1.5° C per minute and the degree of magnetization noted at suitable intervals. In the second method, the procedure consisted in heating a specimen to a definite temperature and holding it at that temperature until the magnetization reached a constant value. This was done at temperatures of 200, 235, and 300 C, with several runs at 400 C.

Figure 1 shows the results obtained by the first method, that is by uninterrupted heating to 300 C of specimens quenched and tempered at 100 C for various periods up to 1,500 hours. The magnetization increased with temperature to a maximum which occurred at 280 C and then decreased with increasing temperature. The maximum was lowered progressively by tempering at 100 C, the change being

[2] R. L. Sanford, Apparatus for thermomagnetic analysis, BS J. Research, 2, 659 (1929); RP 50.

most marked in the early part of the tempering period. The abrupt increase in magnetization took place at higher and higher temperatures as the tempering period was increased.

Figure 2 illustrates the change in hardness as tempering progressed. The part of the curves corresponding to relatively short tempering periods is indicated by dotted lines, as the trend in this region is somewhat uncertain. Several investigators have reported an increase in hardness for quenched specimens tempered for short periods of time at 100 C. In this investigation, no hardness determinations

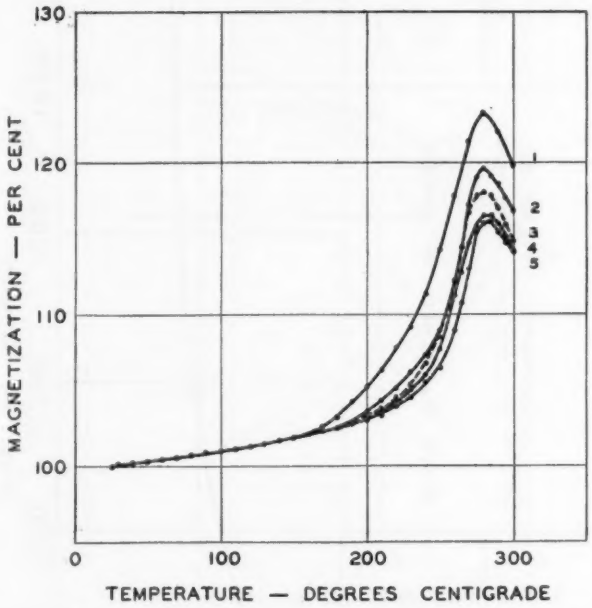

FIGURE 1.—*Effect of prolonged tempering at 100 C upon magnetization*
Details of treatment of each specimen (numbers 1, 2, 3, 4, and 5) are given in table 1.

were made on specimens aged for less than 1 week, at which time the hardness was appreciably lower than that of the quenched material.

Figure 3 is typical of the results of thermomagnetic analysis when the second procedure given above was followed. Here are shown the changes in magnetization which took place upon heating to, holding at, and cooling from a predetermined temperature. The magnitude of the changes observed upon holding at a constant temperature and the time required for the changes to be completed depended upon the treatment to which the various specimens had previously been subjected. All of the other curves were substantially similar in form to those shown.

In this procedure a progressive increase in magnetization took place immediately upon heating, at the rate of increase depending upon the rate of heating. Upon holding at 200 C the magnetization continued to increase over a period of several hours, after which no further increase was noted. On cooling to room temperature little, if any, change in magnetization was observed.

Upon reheating, no appreciable change in magnetization was noted until the temperature was approximately 230 C. On holding at 235 C an increase in magnetization was observed, which continued for approximately 40 minutes. No further change took place upon holding for an hour but in cooling to room temperature, a progressive increase in magnetization was again observed.

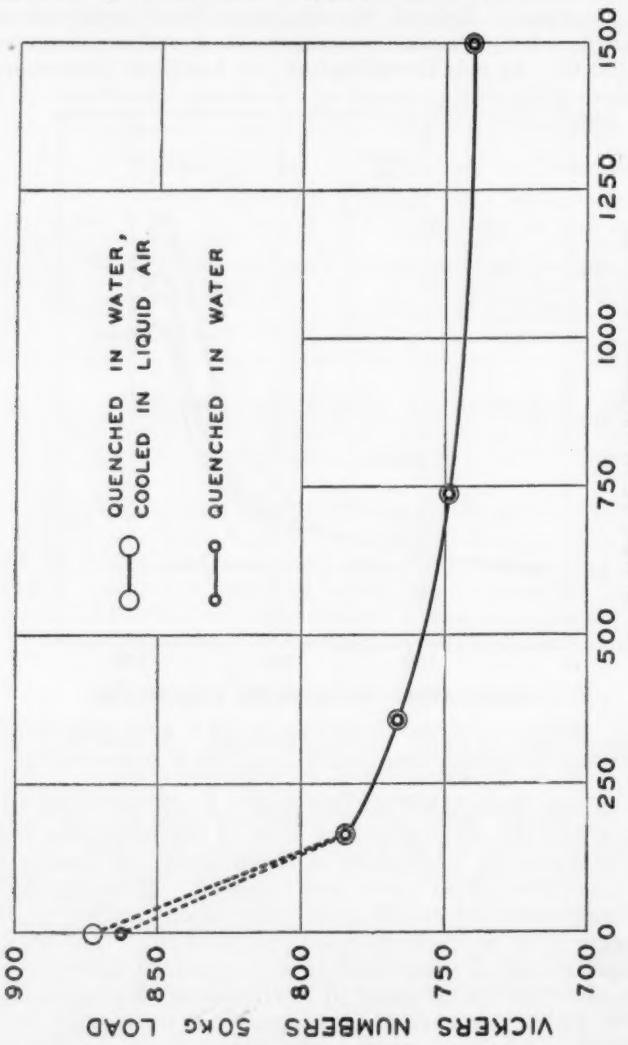

FIGURE 2.—*Effect of prolonged tempering at 100 C upon hardness*

On reheating to 300 C a gradual progressive decrease in magnetization took place, which continued for some time as that temperature was maintained constant. Upon cooling, a pronounced A_o transformation was observed which indicated the presence of cementite. Specimens reheated to 400 C revealed, in no case, any further change in magnetization as the specimen was held at that temperature.

From this type of curve were derived the data shown graphically in figure 4, in which the total changes in magnetization at each of these

temperatures are plotted on a percentage basis. The value for 200 C was the total change upon heating to and holding at that temperature. The values given for the other temperatures were the changes that took place only during the time the temperature was held constant.

The increases in magnetization occurring at 200 C show several features. The maximum increase occurred in freshly quenched specimens (no. 6) while the effect was somewhat less in specimens aged for 2 years (no. 9). Tempered specimens (no. 7) and those tempered and aged (no. 8) showed the least increase, both having practically

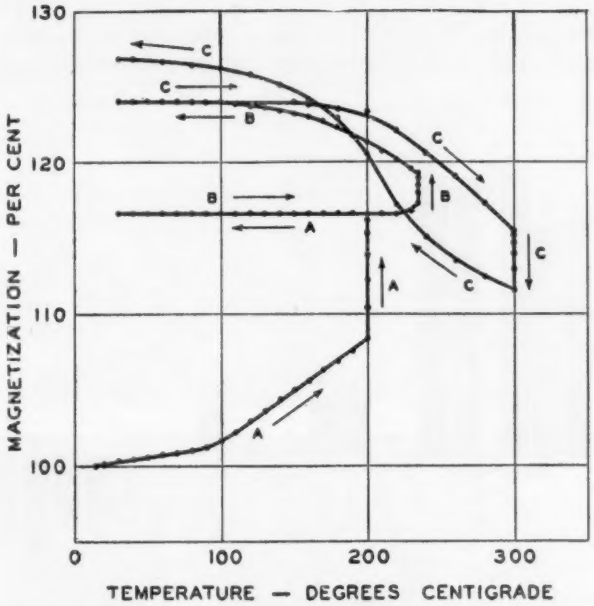

FIGURE 3.—*Typical thermomagnetic curve showing changes in magnetization in quenched steel*

A—Maximum temperature 200 C.
B—Maximum temperature 235 C.
C—Maximum temperature 300 C.

the same value. After treatment with liquid air the increase in magnetization after tempering and aging (no. 11) was the same as that observed immediately after the liquid air treatment (no. 10).

The increase in magnetization observed upon holding the specimens at 235 C was affected by neither the simple liquid air treatment (no. 10) nor tempering (no. 7). Aging for 2 years (nos. 8, 9, and 11), on the other hand, very greatly reduced the change.

The decrease in magnetization occurring when a specimen was maintained at 300 C was apparently affected very little by tempering (no. 7) but aging (nos. 8, 9, and 11) influenced this change materially. The maximum change was noted in the aged specimens regardless of previous treatment. Figure 5 shows the differences in time required for the changes occurring at 300 C, to be completed. Specimens aged 2 years at room temperature (nos. 8 and 9) required more than twice as long for completion of the change as did the freshly quenched

specimens (no. 6). In both cases, the liquid air treatment (nos. 10 and 11) increased the time required.

A study of the microstructure of the quenched and tempered specimens was made. Typical structures are shown in figures 6 to 8, inclusive. The martensite needles showed a progressive darkening as time of tempering increased and a gradual breaking down, particularly in the latter stages, until after 1,500 hours it was difficult to reveal structural details with any degree of sharpness.

IV. DISCUSSION

From the results it is evident that, even at room temperature, quenched steel undergoes progressive changes, the magnitude of which

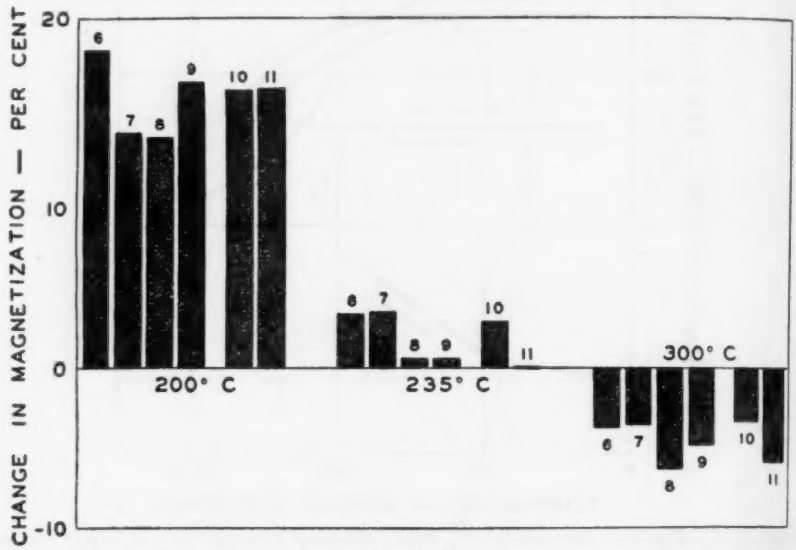

FIGURE 4.—*Changes in magnetization taking place at 200, 235, and 300 C*

Details of treatment of each specimen are given in table 1.

is determined by preliminary treatment such as cooling in liquid air or heating for prolonged periods at 100 C. It is apparent further, that the effect of these changes differs from the "age hardening" phenomena in other metals, but rather is a softening effect.

In considering the changes at 200 C, it was observed that the maximum increase in magnetization occurred in freshly quenched specimens and was least in tempered specimens. These changes have previously [3] been attributed to the gradual release of stresses induced by quenching.

It is known from the results of other investigators that martensite is in a highly stressed state, the stresses being so high as to convert the normal cubic lattice of alpha iron into a pseudo-tetragonal form. Furthermore, martensite is in the state of a super-saturated solid solution, such solution being forced by the extremely rapid cooling with no chance for the precipitation of carbon and the formation of cementite.

Low temperature tempering or sufficiently long aging periods are believed to relieve these stresses materially through the gradual

[3] See footnote 1.

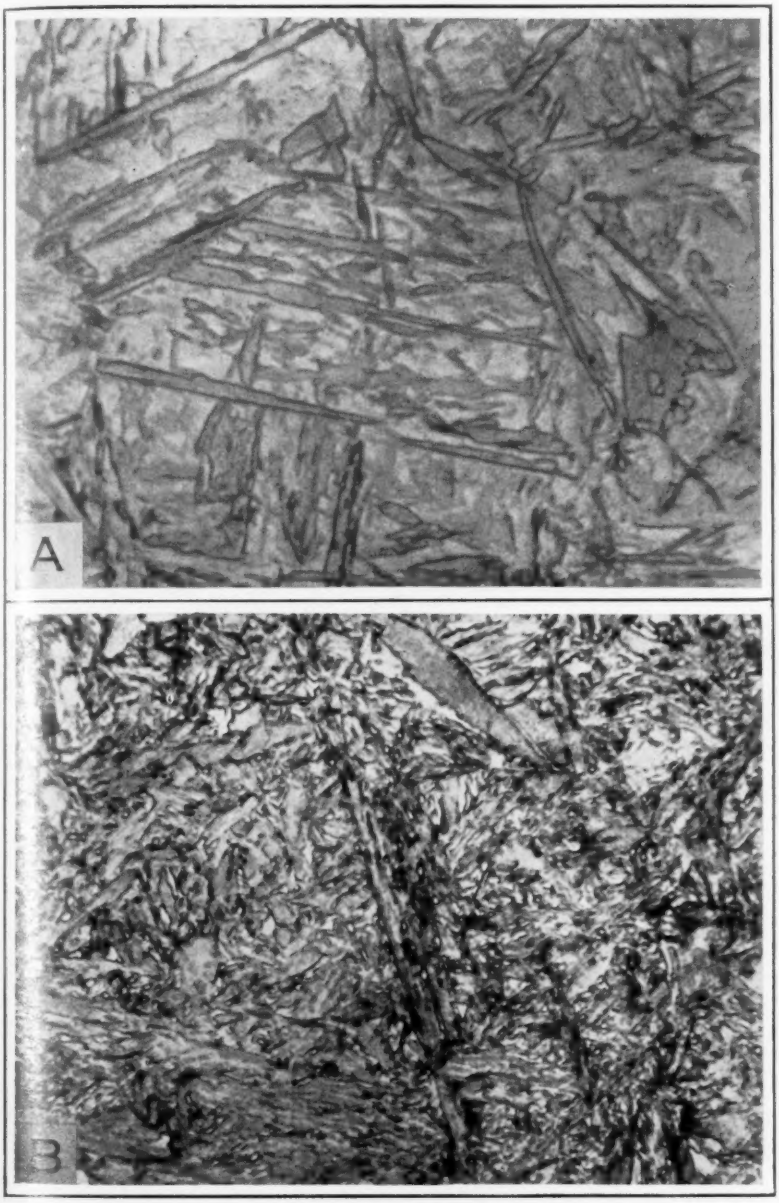

FIGURE 6.—A, *Structure of specimen freshly quenched in water,* × *1500;* B, *structure of specimen after tempering 168 hours at 100° C,* × *1500.*

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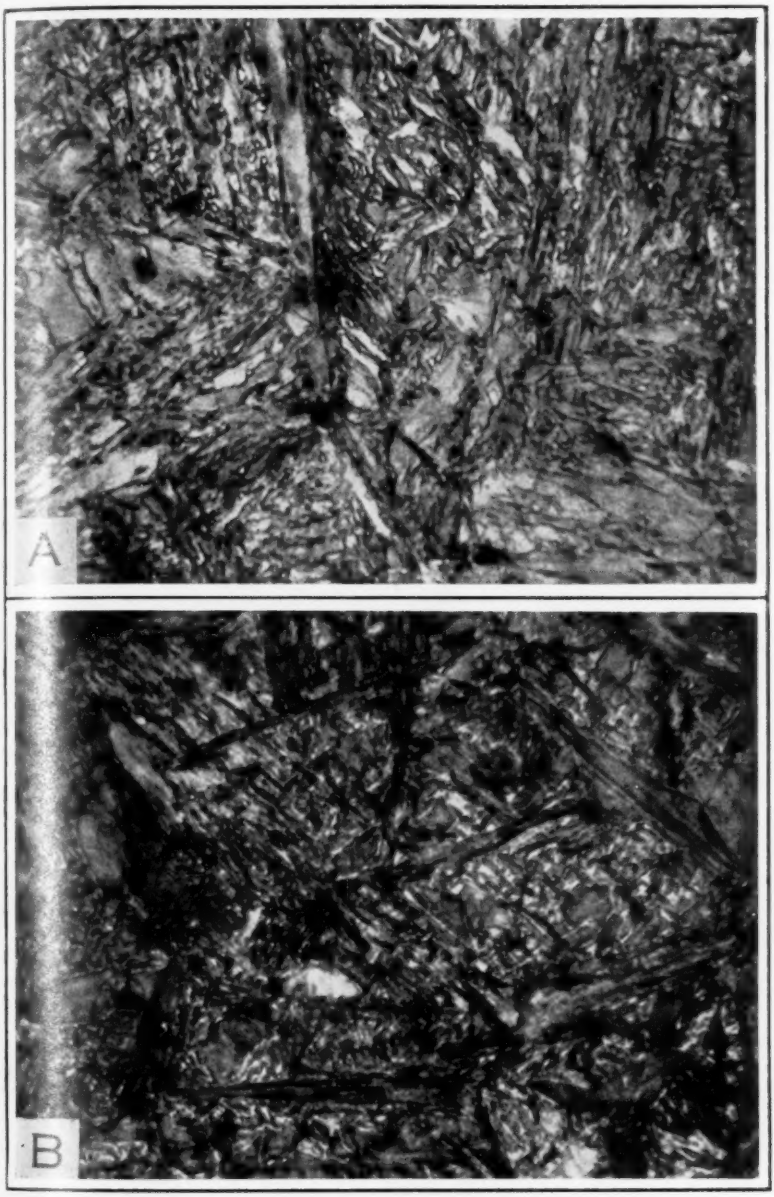

FIGURE 7.—A, *Structure of specimen after tempering 360 hours at 100° C., × 1500;* B, *structure of specimen after tempering 750 hours at 100° C, × 1500.*

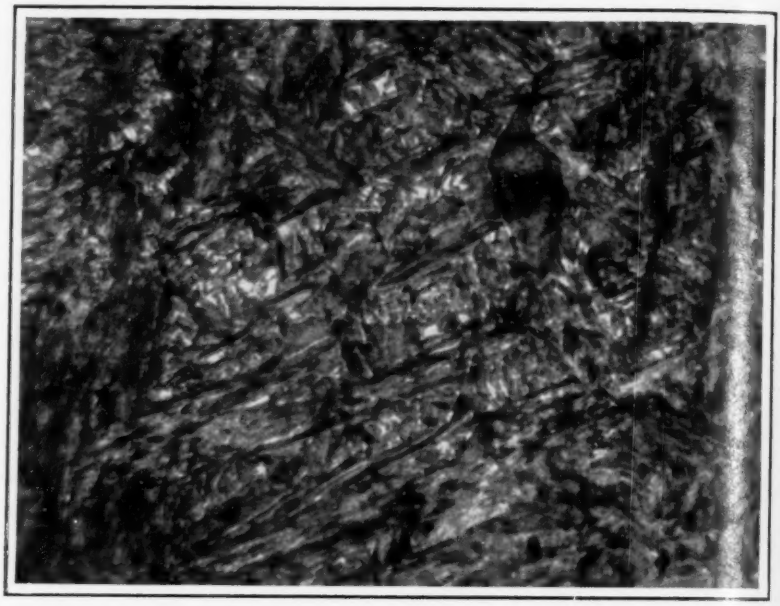

FIGURE 8.—*Structure of specimen after tempering 1500 hours at 100 C,* × *1500.*

precipitation of carbon, either as atomic carbon or some constituent other than cementite. The lattice then assumes more nearly its cubic dimensions with a resultant decrease in hardness. Likewise, the stability of the tempered or aged martensite is increased.

The effect of cooling specimens in liquid air is quite pronounced. The magnitude of the change at 200 C was affected by neither tempering nor aging, which indicates that little significant change took place in the martensite. Greater stresses must have been induced by cooling in liquid air than in water quenching and certain of these stresses must have been released upon subsequently warming to room temperature. This release must have been of considerable magnitude as evidenced by the diminished increase of magnetization at 200 C. The effect of liquid air treatment, not unlike that of tempering, appears to be one of stabilization of martensite. This is further indicated by the fact that tempering and aging apparently have no effect upon the magnitude of the magnetic change at this temperature.

Small amounts of austenite usually exist in freshly quenched steel. This constituent is unstable, being forcibly detained in the undercooled state and will transform to stable phases as soon as permitted. That such was the case is supported by the data. The freshly quenched steel evidently contained an appreciable amount of austenite which decomposed upon heating to 235 C. Even after tempering there was little or no change in the amount of austenite present, but after aging for 2 years this amount was reduced materially. Those specimens which, in the freshly quenched condition, showed the presence of austenite increased somewhat in magnetization upon cooling from 235 C. The nature of the curves, figure 3, suggests that a small amount of cementite was formed at this point, most of which probably came from the decomposition of austenite.

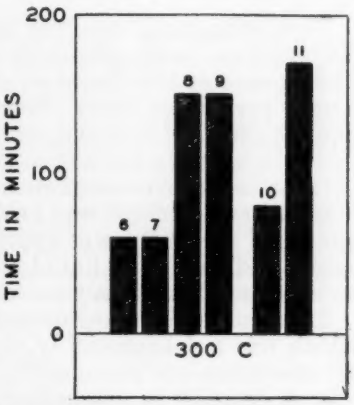

FIGURE 5.—*Time required for decrease in magnetization to be completed at 300 C*

The decrease in magnetization taking place at 300 C is attributed to the formation of cementite by the combination of carbon precipitated from martensite with alpha iron. As this took place above the A_0 transformation temperature of cementite (normally considered as 215 C), that portion of alpha iron which combines with carbon is rendered ineffective magnetically with a resultant net reduction in the total magnetization. A hypothesis was set up previously [4] indicating that in the range from 235 to 300 C atoms of carbon precipitated from the supersaturated martensite solution would unite with atoms of iron to form cementite.

Tempering or cooling in liquid air apparently had little effect upon the magnitude of the changes taking place at 300 C. On the other hand, aging for a considerable period of time produced a noticeable effect. The magnitude of the change and its duration were materially increased.

[4] See footnote 1.

The evidence points to a more rapid formation of cementite from the decomposition products of freshly quenched martensite than from those of aged martensite. The amount of carbide formed depends upon the amount of carbon in the steel and should be the same for a given percentage of carbon regardless of its form. A certain amount was formed while heating to 300 C and the remainder while holding at that temperature. The intensity and duration of the change at 300 C was greater in aged than in freshly quenched specimens. This leads to the belief that in aged specimens less carbide was formed in the range between 235 and 300 C than while holding at 300 C, while in unaged specimens most of the carbide is formed between 235 and 300 C. The sluggishness indicates the possibility that carbon atoms are in less favorable position to unite with iron atoms after aging and require considerably more time for the reaction to take place.

V. SUMMARY

Thermomagnetic analysis has been applied to the study of 0.8 percent carbon steel quenched in water and subsequently tempered 1,500 hours at 100 C and aged at room temperature (0 to 35 C) over longer periods of time. Some quenched specimens were cooled in liquid air for 2½ hours and subsequently tempered and aged. Changes took place during heating of these specimens as follows:

1. An increase in magnetization occurred during the heating of the material and while it was held at 200 C, the magnitude of which, in quenched specimens was appreciably affected by previous tempering, aging, and cooling in liquid air. Tempering and aging had no effect on specimens previously cooled in liquid air.
2. An increase in magnetization occurred in specimens held at 235 C which was not appreciably changed by previous tempering or liquid air treatment but was materially changed by aging.
3. A decrease in magnetization was observed in specimens held at 300 C which was changed appreciably in both magnitude and duration by previous aging.

The explanations offered for the behavior of this material after tempering and aging, based upon observations of changes taking place at various temperatures are as follows:

The carbon of martensite is gradually precipitated both after prolonged tempering at 100 C and after aging, so that the more stable cubic form results. Martensite is also changed by cooling in liquid air but is not further changed by either tempering or aging.

The small amount of austenite retained in 0.8 percent carbon steel after quenching is not affected by tempering but is decreased materially by aging. Liquid air treatment has no apparent effect upon this retained austenite.

Between 235 and 300 C, in what is believed to be the cementite formation range, previous tempering causes no observable difference in magnitude or time. Aging, on the other hand, increases both magnitude and time of the reaction.

The authors wish to express their appreciation and gratitude for the conscientious assistance and cooperation of E. G. Bennett of the National Bureau of Standards, in making many of the determinations in this investigation.

WASHINGTON, June 19, 1934.

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RESEARCH PAPER RP708

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INFLUENCE OF OXIDE FILMS ON THE WEAR OF STEELS

By Samuel J. Rosenberg and Louis Jordan

ABSTRACT

The effect of oxygen-free atmospheres (nitrogen and hydrogen) upon the wear of a hypoeutectoid, a eutectoid, and a hypereutectoid carbon steel was studied. It was found that when these steels were hardened and subsequently tempered at low temperatures, the rates of wear were comparatively low; the wearing surfaces were smooth and were covered by a thin oxide film and the abraded particles consisted of Fe_2O_3 and Fe_3O_4. When these steels were tempered above certain temperatures, the rates of wear were extremely high; the worn surfaces were very rough and bright and the abraded particles were metallic iron.

Microscopic examination showed that those steels which had rough, film-free worn surfaces had severely distorted structures adjacent to these surfaces. In the case of steels which showed only the filmed, worn surfaces, the structures adjacent to these surfaces were not greatly changed by the wear test and the worn surfaces themselves were smooth. The severely distorted structure was also observed in the case of certain steels which showed characteristics of both types of wear. Numerous cracks intersecting or approximately parallel to the worn surfaces were observed in the microexaminations of both types of surfaces.

These tests indicated that a film of either ferric or ferroso-ferric oxide on the wearing surfaces of carbon steels results in a certain degree of protection against wear, probably by preventing actual metal-to-metal contact. When these films are absent, severe wear of a galling type takes place.

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I. INTRODUCTION

Marked advances in many phases of the testing of metals have taken place in recent years, yet little or no real progress in developing the fundamentals of the wear testing of metals has been achieved. This is probably because of the complexity of this particular problem, the difficulty in separating the numerous factors of service conditions which influence wear, and the consequent difficulty in properly understanding and evaluating the individual effects of these factors upon the mechanism and nature of wear.

The logical method of attacking the general problem of wear of metals is to attempt to separate these factors which occur in service and to study the effect of each upon the wear. The factor selected for study and reported in this paper is that of the effect of the presence or absence of oxygen in the atmosphere surrounding the wearing surfaces of metals.

The appearance of films upon the wearing surfaces of metals has frequently been observed. It has been accepted that these films influenced the results obtained in wear testing; in some cases attempts have been made to minimize or prevent the formation of films by

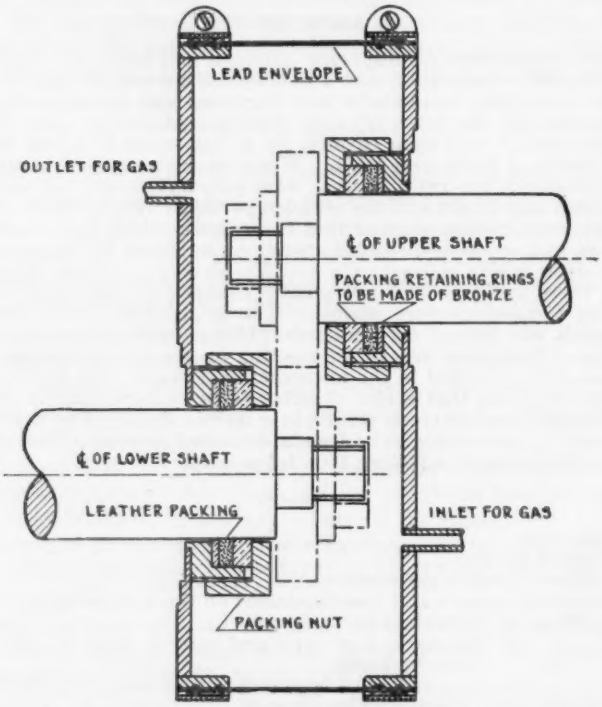

FIGURE 1.—*Details of cell used to maintain the desired atmosphere around the wear-test specimens*

mechanical means, while in other cases the films have been allowed to form and remain on the assumption that they are a natural phase of the wearing process.

An hypothesis as to the effect of oxide films upon the wear of metals has been advanced by Fink,[1] as a result of tests on steel in oxygen-free atmospheres. The wearing surfaces at the conclusion of his tests were very smooth and shiny and the specimens had suffered no wear. When the same steels were tested in air, the surfaces were covered with oxide films and an appreciable amount of wear took place. This phenomenon of film formation Fink terms "wear oxidation" and, according to his theory, oxygen is essential if wear is to take place between two metallic surfaces.

[1] Max Fink, "Wear oxidation; a new component of wear", Trans. Am. Soc. for Steel Treating, vol. 18, p. 1026, 1930 (see also "Neue Ergebnisse auf dem Gebiet der Verschleissforschung," Organ für die Fortschritte des Eisenbahnwesens, vol. 66 ,p. 405, Oct. 15, 1929).

II. METHODS OF TESTING

An Amsler wear-testing machine (the same type as used by Fink) was used for the tests described in this paper. In this machine wear takes place on the circumferences of 2 specimens 2 in. in diameter and 0.4 in. thick, mounted on parallel horizontal shafts as shown in figure 1. An oval cell to inclose the specimens and maintain the desired atmosphere during test was constructed as also shown in figure 1.

The cell was closed for each test with a strip of lead foil about 0.006 in. thick. This foil was pressed tightly against the grooved circumference of the brass side walls of the cell by means of two rubber gaskets and two brass strips which could be tightened by means of a screw. The lapped joint in the lead envelope was sealed with a mixture of beeswax and rosin.

Hydrogen was used for the oxygen-free atmosphere in the majority of the tests. Nitrogen was used in a few tests. Both gases were purified in the train shown in figure 2. The rate of flow of gas, observed from the bubbles through the sulfuric acid, was kept fairly rapid in order to maintain a pressure slightly above atmospheric within the cell. The purified gas was allowed to flow through the

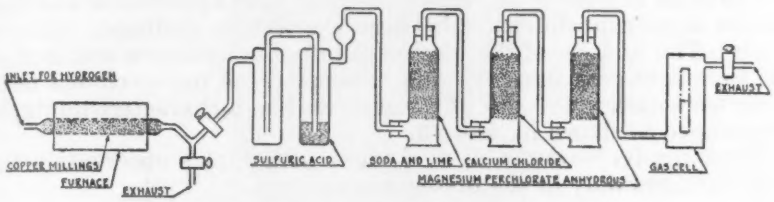

FIGURE 2.—*Train for purifying and drying gas*

cell for at least 15 minutes before starting each run. Gas analyses, sensitive to 0.03 to 0.04 percent oxygen, failed to indicate the presence of oxygen in the gas leaving the cell.

The test specimens were washed in carbon tetrachloride, dried, and weighed before and after each test; the losses in weight were used as a measure of the wear. The oscillating motion of the upper head of the Amsler machine was not used in any of the tests.

III. REPETITION OF FINK'S EXPERIMENTS

An effort was first made to duplicate the results reported by Fink. He tested a 0.65 percent carbon steel, having an ultimate tensile strength of approximately 115,000 lb/in.,[2] in an atmosphere of nitrogen under a load of 59 kg and with 1 percent slip. Of the steels available, that most nearly approximating 0.65 percent carbon had the following composition:

	Percent
C	0.58
Mn	.29
P	.014
S	.018
Si	.27

Slip of approximately 1 percent between the wearing surfaces was obtained by mounting a specimen of 2.186 in. diameter on the upper shaft of the machine and one of 2.0 in. diameter on the lower shaft.

All of the specimens were normalized at 825 C, water quenched from 800 C and tempered at 625 C. This heat treatment gave a Brinell hardness number of 230, which corresponds to a tensile strength of approximately 110,000 lb/in.[2]

Results of tests made under these conditions in atmospheres of hydrogen, nitrogen, and air are summarized in table 1.

TABLE 1.—*Wear of 0.58 percent C steel in different atmospheres under 50 kg load and 1 percent slip*

Atmosphere	Specimen	Rate of wear—Loss in grams per 10,000 revolutions of lower specimen
Air	Upper	0.08
	Lower	.05
Nitrogen	Upper	.09
	Lower	.07
Hydrogen	Upper	.06
	Lower	.05

The rates of wear of all these specimens were appreciable and there was no significant difference between the tests in hydrogen, nitrogen, or air. The surfaces of the specimens tested in hydrogen and in nitrogen were light gray in color, while the surfaces of the specimens tested in air were dark gray. All of the surfaces had a characteristic rippled appearance as shown in figure 3.

These results were not in agreement with Fink's observation that wear occurred only in the presence of oxygen.

IV. EFFECTS OF ATMOSPHERE AND HEAT TREATMENT ON THE WEAR OF STEELS

1. WEAR OF A EUTECTOID CARBON STEEL

(a) COMPARISON OF TYPE AND RATE OF WEAR IN DIFFERENT ATMOSPHERES

Eutectoid carbon steel (0.81 percent carbon) was chosen for further study of the effect of atmosphere upon wear The first tests of this steel in atmospheres of hydrogen and of nitrogen were made under 60 kg load and 10 percent slip and with specimens which had been hardened and subsequently tempered at 260 C (details of composition and heat treatment are given in table 4).

Worn surfaces which were smooth and covered by a reddish-brown film, sometimes streaked with black, were produced by these tests. The frictional torque was high, about the same as when identical specimens were tested in air, and the rate of wear was generally somewhat lower than when similar specimens were tested in air. (See table 2.) It was rather surprising that the wearing surfaces were covered with films, apparently of oxides, when tested in "oxygen-free" hydrogen or nitrogen. A probable explanation of this phenomenon is advanced in a later section of this paper.

In all these cases both the upper and lower specimens had been tempered at 260 C. In a subsequent test, however, a specimen which had been tempered at 400 C was inadvertently tested against one tempered at 260 C. The results in this case were markedly different.

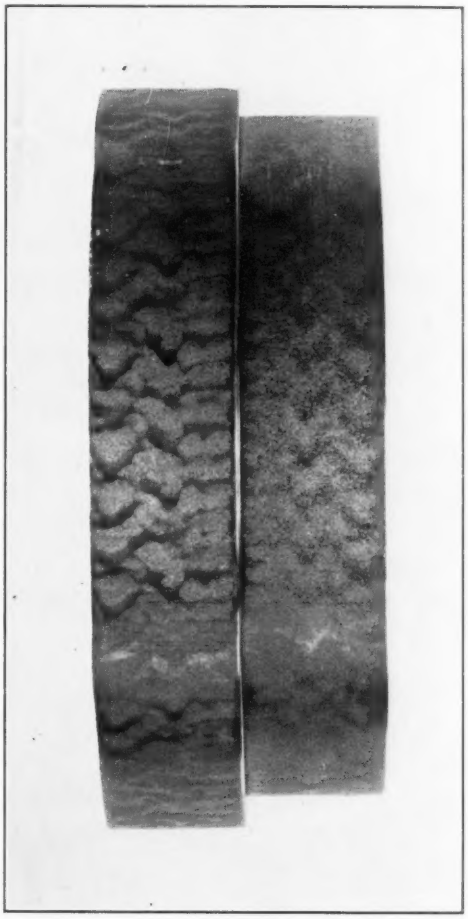

FIGURE 5.—*Worn surfaces of steels tested in hydrogen under 50 kg load and 1 percent slip.* × 1¾.

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The wearing surfaces of both specimens were bright with no trace of film; they were also very rough and the wear of the specimen tempered at 400 C was relatively enormous. The wear rates per 10,000 revolutions were as follows:

	Grams
Upper specimen (tempered at 400 C)	8. 5
Lower specimen (tempered at 260 C)	0. 28

Additional tests, in both oxygen-free hydrogen and in moist hydrogen, of specimens tempered at 400 C gave excessively high wear rates and rough, film-free surfaces. When specimens tempered at 260 C were tested in air, the wear rate was 0.03 gram and when both were tempered at 400 C, the rate was 0.06 gram. In both of these cases the surfaces were smooth and filmed. The frictional torque developed during the tests in hydrogen was lower than when specimens of the same steel treated in the same way were tested in air. A photograph of specimens showing the "smooth, filmed" type of worn surface and the "rough, bright" type of worn surface after testing in hydrogen is shown in figure 4. These two groups of specimens (one tempered at 260 C and the other at 400 C) were also tested in oxygen.

Table 2 summarizes the results of all of these tests. There were no significant differences between the effects of any of the media surrounding the specimens tempered at 260 C. The wear rates of these specimens were low in all five atmospheres; the worn surfaces were smooth and filmed. In the case of the specimens tempered at 400 C the results of the tests in air were similar to the results obtained in all types of atmospheres with the specimens tempered at 260 C, i.e., the surfaces were smooth and filmed and the wear rates were low. When specimens tempered at 400 C were tested in hydrogen atmospheres, however, the wear rates were high and the surfaces were rough and bright. This effect was noted in both moist and dry hydrogen.

TABLE 2.—*Tests of 0.81 percent carbon steel in different atmospheres*

[60 kg load—10 percent slip]

Tested in—	Wear rate—Loss in grams per 10,000 revolutions	
	Tempered at 260 C	Tempered at 400 C
Hydrogen	0.001–0.02 (16 determinations)	0.4–16.0 (8 determinations).
Moist hydrogen	0.01 (2 determinations)	0.2 (2 determinations).
Nitrogen	0.004–0.008 (2 determinations)	
Oxygen	0.03 (2 determinations)	
Air	0.03 (2 determinations)	0.06 (2 determinations).

NOTE.—Each value represents the slope of a weight-loss-revolutions curve of a separate specimen determined by a series of wear tests, each of which ran for 10,000 revolutions. The values given are the minimum and maximum obtained.

(b) COMPARISON OF TYPE AND RATE OF WEAR AFTER DIFFERENT TEMPERING TREATMENTS

The marked change observed in the preceding tests in both the type and rate of wear raised the question whether this change occurred gradually with increasing tempering temperature, or whether the transition occurred abruptly. A series of specimens tempered at various temperatures was therefore tested in hydrogen and in air. All these specimens were 0.81 percent carbon steel except the specimens tempered at 150 C, which were 0.88 percent carbon steel. The results of these tests are summarized in table 3.

TABLE 3.—*Effect of tempering temperature on the wear of carbon steels in different atmospheres*

[60 kg load—10 percent slip]

0.81 PERCENT CARBON STEEL

Tested in—	Wear rate—Loss in grams per 10,000 revolutions									
	Not tempered	Tempered at 150 C	Tempered at 200 C	Tempered at 230 C	Tempered at 260 C	Tempered at 290 C	Tempered at 320 C	Tempered at 360 C	Tempered at 400 C	Tempered at 500 C
Hydrogen		0.003–0.02 (4 determinations)[1]. Smooth, filmed.			0.001–0.02 (4 determinations). Smooth, filmed.	0.01–0.02 (4 determinations). Smooth, filmed.	2.0–4.0 (2 determinations). Rough, bright.	0.2–0.4 (2 determinations). Rough, bright.	0.4–16.0 (8 determinations). Rough, bright.	
Air					0.03 (2 determinations). Smooth, filmed.		0.03–0.05 (2 determinations). Smooth, filmed.	0.05–0.10 (2 determinations). Smooth, filmed.	0.06 (2 determinations). Smooth, filmed.	

0.43 PERCENT CARBON STEEL

Hydrogen	0.002–0.016 (4 determinations). Smooth, filmed.		0.10 (2 determinations). Rough, bright during first run. Smooth, filmed during succeeding runs.	0.12 (2 determinations). Type of wear alternated between rough, bright and smooth, filmed.	0.23–0.31 (2 determinations). Rough, bright during first few runs. Smooth, filmed during last two runs.		0.34–0.44 (2 determinations). Rough, bright during first few runs. Type of wear alternated during last three runs.			
Air			0.04–0.06 (2 determinations). Smooth, filmed.	0.07–0.09 (2 determinations). Smooth, filmed.	0.08–0.09 (2 determinations). Smooth, filmed.		0.11–0.15 (2 determinations). Smooth, filmed.			

Hydrogen					0.007–0.014 (2 determinations). Smooth, filmed.				0.01–0.1 (4 determinations). No films during first run in each test. Film formed during second run and remained.	0.8–4.2 (2 determinations). Rough, bright.
Air										0.03–0.1 (2 determinations). Smooth, filmed.

[1] This steel contained 0.88 percent carbon.

They show that a "critical" range of tempering temperatures exists in the 0.81 percent carbon steel between 290 and 320 C. Specimens tempered above this temperature range and tested in hydrogen had rough, bright worn surfaces and the rate of wear was extremely high as compared with the rate in air. Specimens tempered below this temperature range and tested in hydrogen had smooth, filmed worn surfaces; the rate of wear was usually lower than that obtained upon testing in air and the films formed were usually considerably lighter in color.

2. WEAR OF A HYPOEUTECTOID AND A HYPEREUTECTOID CARBON STEEL

Similar tests were made on a hypoeutectoid carbon steel (0.43 percent carbon) and a hypereutectoid carbon steel (1.26 percent carbon) to determine whether the wear phenomena observed in the eutectoid steel would also be evident in steels of lower and higher carbon content.

The data obtained in the tests on these steels are also given in table 3. The same general effects of atmosphere and tempering temperature were evident in these steels, that is, a critical range of tempering temperatures existed in each steel. The "critical" tempering range was lower (between 200 and 230 C) for the hypoeutectoid steel and was higher (between 400 and 500 C) for the hypereutectoid steel than for the eutectoid steel. As in the case of the eutectoid steel, the rates of wear of these steels in air increased but slightly with increase of tempering temperature; the type of wear remained the same in all tests in air.

3. SUMMARY OF THE WEAR TESTS

A general summary of the significant features of the wear tests in oxygen-free hydrogen is presented in table 4. The compositions and heat treatments of the steels are also given in this table.

TABLE 4.—*Summary of the wear of steels in hydrogen*

[60 kg load, 10 percent slip]

Composition (percent)	Heat treatment	Tempering temperature	Rockwell "C" number	Type of worn surface	Rate of wear
C 0.43 Mn .68 P .031 S .038 Si .28	Water quenched from 835 C	°C None.	58	Smooth, filmed	Low.
		200	53	Borderline	
		230	52	do	
		260	50	Rough, bright, clean	High.
		320	48	do	Do.
C 0.81 Mn .23 P .024 S .021 Si .28	Normalized 810 C; water quenched from 770 C.	• 150	64	Smooth, filmed	Low.
		260	58	do	Do.
		290	56	Borderline	
		320	54	Rough, bright, clean	High.
		360	47	do	Do.
		400	45	do	Do.
C 1.26 Mn .39 P .024 S .018 Si .28	Normalized 925 C; annealed 760 C; water quenched from 770 C.	260	50	Smooth, filmed	Low.
		400	48	Borderline	
		500	39	Rough, bright, clean	High.

• Steel used for this treatment contained 0.88 percent C.

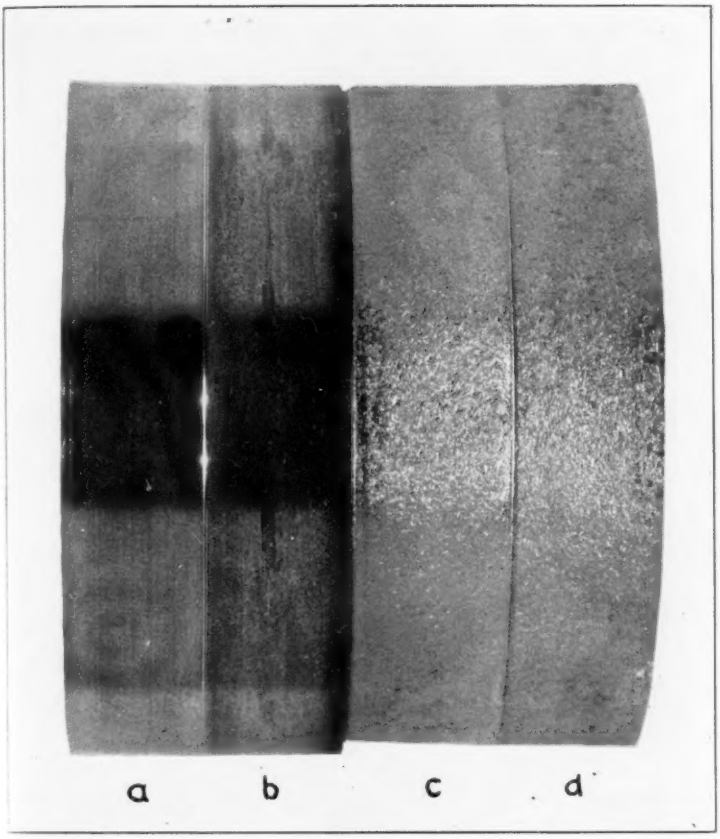

FIGURE 4.—*Worn surfaces of steels tested in hydrogen under 60 kg load and 10 percent slip.* $\times 1\frac{1}{4}$.

a and b, Smooth, filmed surfaces; c and d, bright, rough, film-free surfaces.

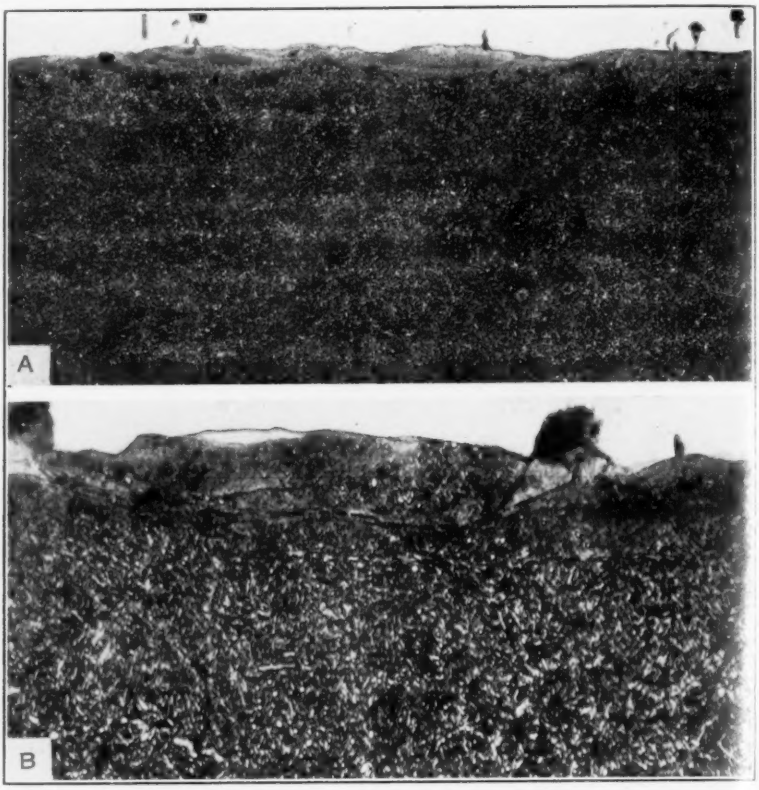

FIGURE 5.—A, *Structure adjacent to rough, film-free, worn surface of a specimen tested in hydrogen.*

Note cold-worked surface layer. (Steel—0.81 percent carbon, water quenched from 770° C and tempered at 230° C. Rockwell C number 52.6.) × 100.

B, *Same specimen as* A, *but another area.*

Note cracks beneath the surface outlining a lenticular area in the initial stages of separating from the wearing surface. × 500.

Both etched with 1-percent nitric acid in alcohol.

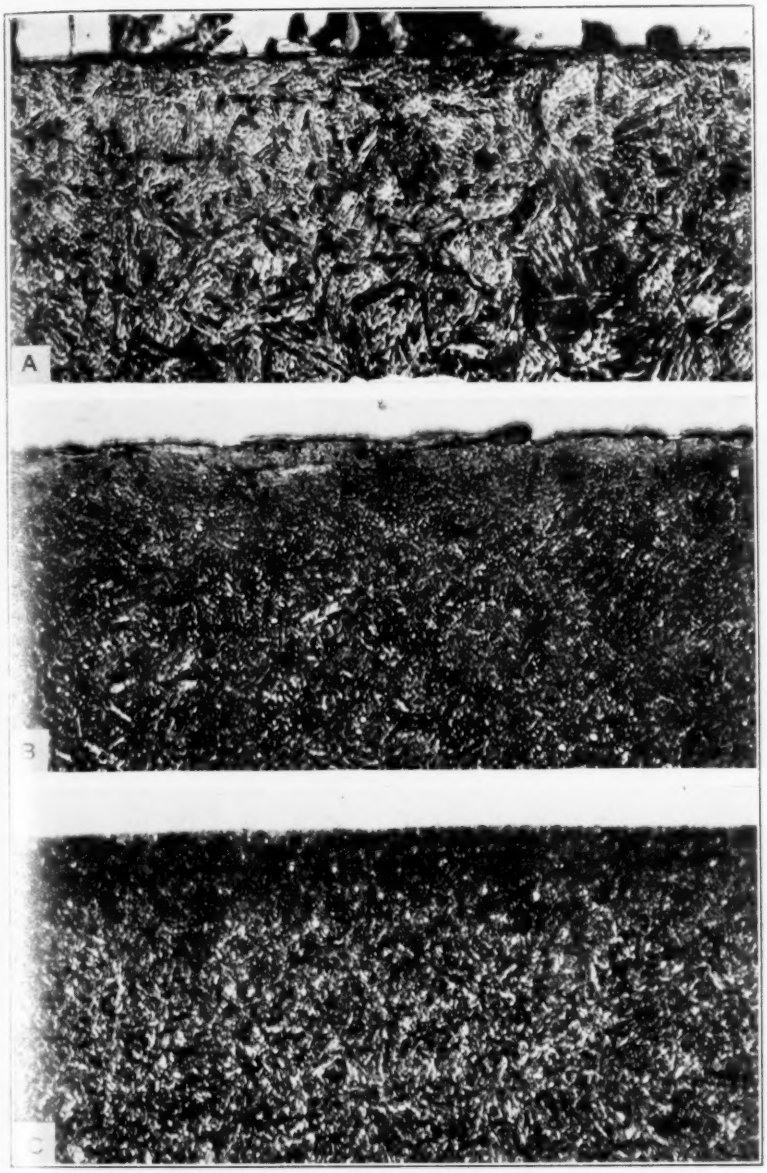

FIGURE 6.—A, *Structure adjacent to the smooth, filmed, worn surface of a specimen tested in hydrogen.*

The martensitic needles are deformed just below the surface. (Steel—0.43 percent carbon, water quenched from 835° C and not tempered. Rockwell C number 58.2.)

B, *Structure adjacent to the wearing surface of a specimen tested in hydrogen.*

This specimen had a rough film-free surface during the first test. In subsequent tests, the surface became filmed. Note cracks beneath and parallel to the wearing surface. (Steel—0.81 percent carbon, water quenched from 770° C and tempered at 290° C. Rockwell C number 56.2.)

C, *Structure adjacent to the smooth, filmed, worn surface of a specimen tested in air.*

Note cracks beneath and parallel to the wearing surface. (Steel—0.81 percent carbon, water quenched from 770° C and tempered at 320° C. Rockwell C number 54.1.)

All × 500. All etched with 1 percent nitric acid in alcohol.

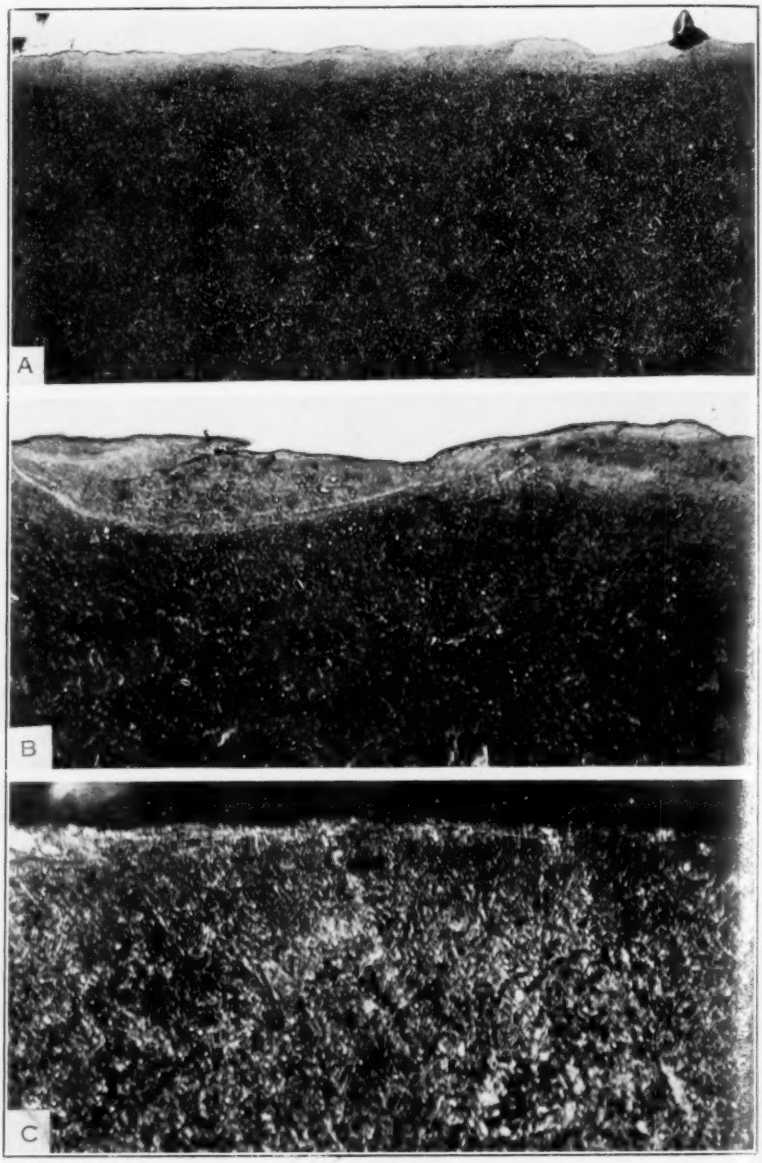

FIGURE 7.—A, *Structure adjacent to the worn surface of a specimen tested in hydrogen.*

The part of the surface shown here was roughened, but filmed. Note cold-worked layer. (Steel—0.81 percent carbon, water quenched from 770° C and tempered at 260° C. Rockwell C number 59.1.) × 100.

B, *Same location as* A.

Note cracks in cold-worked layer. × 500.

C, *Same specimen as* A, *but showing structure adjacent to the smooth filmed surface.*

All etched with 1 percent nitric acid in alcohol. × 500.

It is worthy of note that under the conditions of loan and slip employed in these tests, steels treated to a Rockwell "C" number of about 56 or higher invariably showed the smooth, filmed type of worn surface in oxygen-free atmospheres. Steels softer than this value had either a border line or a rough, film-free type of worn surface.

V. MICROSTRUCTURAL CHARACTERISTICS OF THE STEELS ADJACENT TO THE WORN SURFACES

Several representative specimens were subjected to a microscopic examination after the wear tests. In the following discussion of the microstructural characteristics the phrase "structure at the surface" is used to indicate not only the regularity of the contour of the actual surface but also the structure of a relatively thin layer of metal immediately below the surface; the phrase "interior structure" designates the structure of the steel at a distance below the worn surface, where it was not affected by the wear test.

Two characteristic types of structures were found adjacent to the worn surfaces. Specimens having the rough, film-free type of worn surface after testing in oxygen-free atmospheres had severely cold worked surface layers. Numerous cracks, evidently caused by the stresses developed during the wear tests, were present at and just below the wearing surfaces. Areas of severely distorted metal frequently lenticular in section and outlined by cracks, were characteristic of the surface structure (see fig. 5).

Specimens having the smooth, filmed type of worn surface after testing either in air or in oxygen-free atmospheres showed a relatively smooth contour of the wearing surfaces under the microscope (see fig. 6 a and c). There was but little evidence of distortion of the layers immediately below the surfaces except for some cracks approximately parallel to the wearing surfaces.

Some specimens started wearing with rough, film-free surfaces but as the tests progressed formed surface films. This type of wear is designated as a borderline type. Micro examinations of such specimens showed that the surface structures characteristic of wear producing a rough, bright surface were still very evident after the surfaces had become covered with films (see figs. 6 b, 7 a and b).

The structures shown in figure 7 a and b were rather unusual with respect to the type of surface developed in the wear tests. All the way around the specimen in the middle of the wearing surface there was a somewhat roughened, although filmed, area. On both sides of this roughened surface was a relatively smooth, filmed surface. This specimen might have been expected, on the basis of the preceding tests, to have had a smooth, filmed, worn surface because of its low tempering temperature. The interior structure of this specimen etched somewhat darker below the rough surface (fig. 7 b) than below the smooth surface (fig. 7 c). This suggests that for some reason the interior structure was more troostitic and therefore slightly softer below the rough, worn surface than below the smooth, worn surface. This may have been the reason for the two different types of wear observed on this specimen.

A very interesting phenomenon developed during the tests of the 0.88 percent carbon steel in hydrogen. After the first test in hydro-

gen, four heavily worn areas appeared on the wearing surface of one of the specimens. Whereas this specimen, due to its low tempering temperature, had the smooth, filmed type of worn surface, these spots were rough, even though they were covered by a thin film. Their appearance was quite similar to that of specimens which normally exhibited film-free, heavily worn surfaces at first and then formed a film either because of an imperfection in the hydrogen gas train or for other causes which will be discussed later. The locations of these rough spots were marked, the specimen was resurfaced and tested again. The spots reappeared in the same locations and with the same shapes as before. Their appearance is shown in figure 8. Rockwell "C" scale readings, made at the locations indicated, are given in this figure.

Apparently these four areas were soft spots, the hardnesses of which were about equal to or lower than the hardness of the eutectoid steel specimens which showed the borderline type of wear in hydrogen. This lower hardness was apparently the cause of the development of the rough areas in an otherwise smooth, worn surface.

Figure 9 shows the structures at the wearing surface of a section cut through one of these rough areas. The worn surface is irregular and shows a thin layer of severely deformed material containing cracks. The interior structure consists of troostite, tempered martensite and free carbides. The presence of the troostite explains the lowered hardness. Figure 10a shows the transition from the rough to the smooth worn surface; it is evident that this transition coincides with the disappearance of the troostitic areas. The structure at the wearing surface of the material which is free from primary troostite is shown in figure 10 b. The wearing surface here was smooth.

VI. NATURE OF THE PARTICLES ABRADED FROM THE SPECIMENS

The abraded particles produced during each test varied with the type of wear. When smooth, filmed surfaces resulted from wear, the amount of abraded particles was small and the color was very dull gray or brownish-black, usually the latter. When bright, rough, film-free surfaces were formed, the amount of abraded particles was large and the color was a very bright gray with no trace of either red or black.

Two samples of abraded particles were examined by X-rays using the powder method and Mo Kα radiation, to determine whether they were iron or iron oxide.[2] One sample (A) consisted of the red and reddish-black particles from the smooth and slightly filmed surfaces formed in testing in an atmosphere of hydrogen 2 specimens of 0.81 percent carbon steel tempered at 260 C. The other sample (B) consisted of bright, light-gray particles from the extremely rough and bright surfaces formed in testing in an atmosphere of hydrogen 2 specimens of 0.81 percent carbon steel tempered at 320 C.

Sample A consisted of Fe_2O_3 and Fe_3O_4. Neither free FeO nor free iron was detected. Sample B gave the pattern of highly distorted iron; no lines representing iron oxides were present. This was not

[2] The authors are indebted to F. Sillers, jr., Research Associate at the National Bureau of Standards for these X-ray examinations.

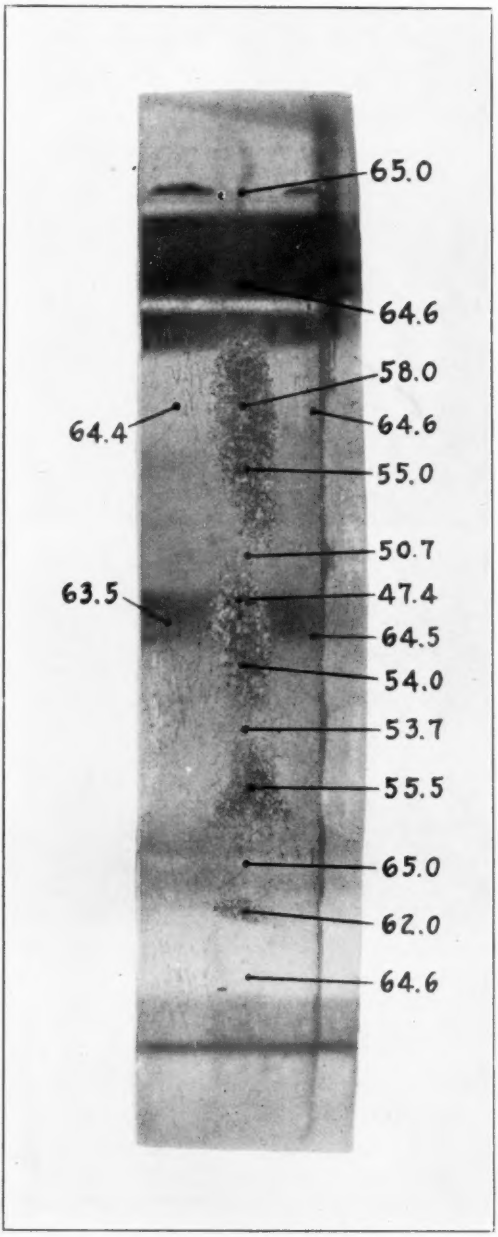

FIGURE 8.—*Specimen showing heavily worn areas after testing in hydrogen.*

(Steel—0.88 percent carbon, water quenched from 770° C and tempered at 150° C. Rockwell C number 64.1.) × 3.

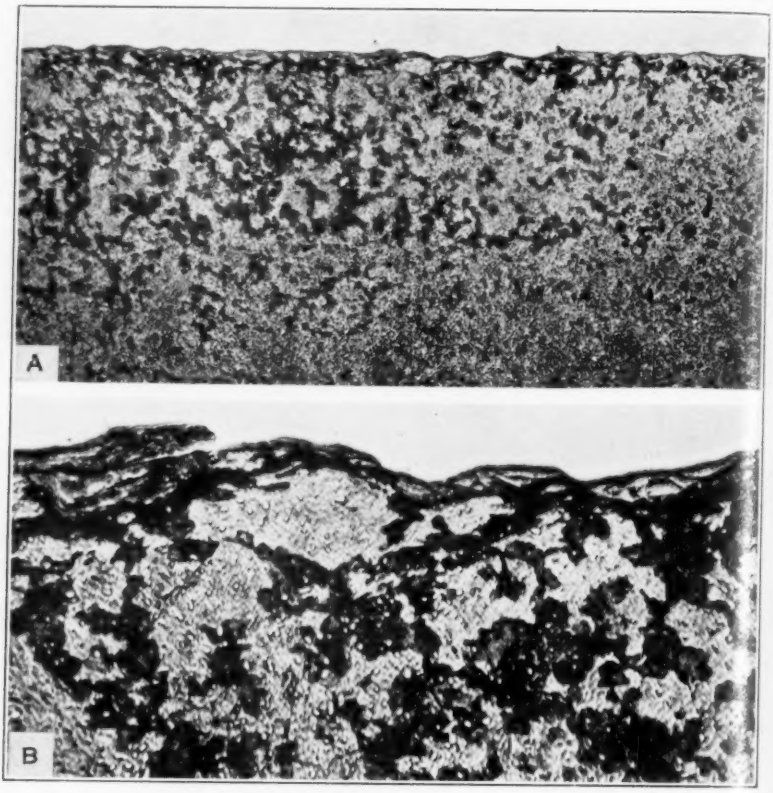

FIGURE 9.—A, *Structure adjacent to the worn surface of a section through one of the rough areas of the specimen shown in figure 8.*

The presence of primary troostite is evidence of incomplete hardening. Note the rough, deformed surface layers. × 100.

B, *Same location as* A.

Note the metallic particle partially separated from the wearing surface. × 500.

Both etched with 1 percent nitric acid in alcohol.

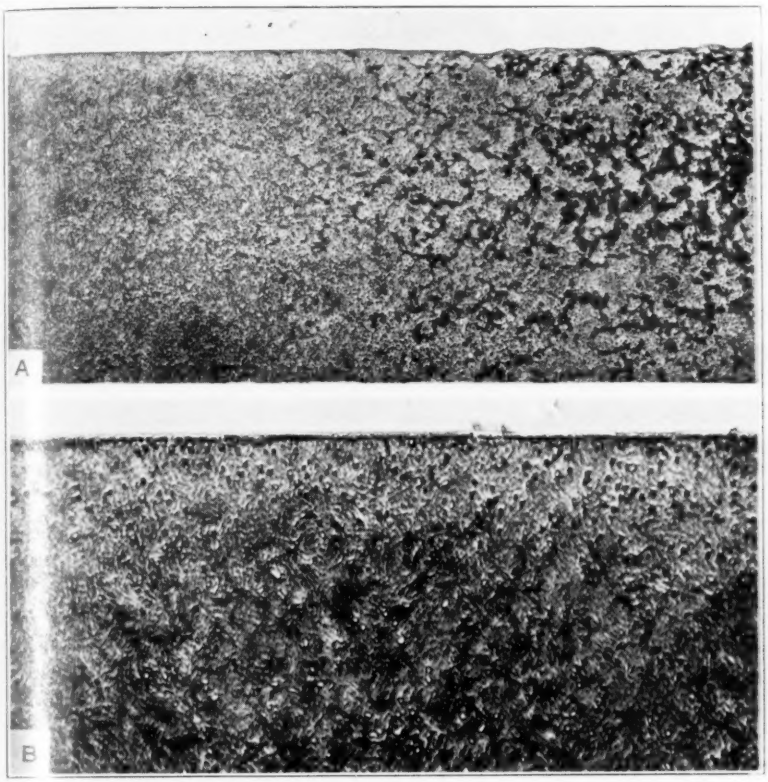

FIGURE 10.—A, *Same specimen as figure 8, showing the transition from the rough to the smooth, worn surface.*

This transition zone is also marked by the disappearance of the troostitic areas. × 100.

B, *Same specimen as figure 8; showing the structure adjacent to the smooth, filmed, worn surface.*

The structure is tempered martensite with a few free carbides. × 500.

Both etched with 1 percent nitric acid in alcohol.

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evidence, however, that very thin oxide films were not present on the surfaces of these particles, since such thin films would not be detected by the X-ray examination.

These results confirmed the supposition that the films formed in "oxygen-free" atmospheres under conditions producing smooth, filmed, worn surfaces were indeed oxide films.

VII. DISCUSSION

Evidence has been gathered during this work definitely contradictory to Fink's conclusion that no wear takes place between two metallic surfaces unless oxygen is present in the surrounding atmosphere. On the contrary, the absence of appreciable amounts of oxygen in the atmosphere surrounding many of the steel specimens tested was conducive to greatly increased wear. The apparent explanation is that there is no opportunity for the wearing surfaces to become covered with a protective oxide film which prevents actual metal-to-metal contact.

It is to be noted that the carbon steels tempered at the lower temperatures formed oxide films even when tested in gases (hydrogen or nitrogen) substantially free from oxygen. It was impossible to remove all traces of oxygen from the interior of the cell used in the wear tests by flushing the cell with purified gas. When 2 specimens are worn against each other, as in the Amsler machine, a fresh, chemically active surface is probably produced which combines readily with any traces of oxygen in the cell. The frictional heat generated at the surfaces of contact naturally tends to assist this reaction. Thin oxide films can, therefore, form on the specimens even in the "oxygen-free" gas.

The question arises why the same process does not occur with the carbon steels tempered at the higher temperatures. It probably does, but apparently the film which forms on these steels is not able to prevent seizing and galling and the resultant excessive wear. The lack of protective action of the oxide film in such instances may be dependent on the physical properties of the steels.

It has been pointed out that the steels which developed smooth, filmed surfaces in an atmosphere of hydrogen were those which had high hardness numbers and the steels which developed rough, bright, film-free surfaces had lower hardness numbers. In the discussion of the microstructures it was shown that a rough surface contour with a very severely distorted layer beneath was a characteristic of the film-free, worn surface. The softer steels, when subjected to wear, deformed under the influence of the various stresses and it is postulated that the oxide film which initially formed was immediately ruptured because of the deformation of the surface on which it formed. The ruptured film permitted actual metal-to-metal contact, seizure over small local areas, and finally, galling and excessive wear.

This deformation was not so apparent in the steels having a smooth, filmed, worn surface. Here it is postulated that the steel had sufficient strength to resist the stresses developed during the wearing action and the oxide film had a firm base upon which to form. Once formed, this film maintained its continuity and further wear, as a rule, failed to destroy it. True metal-to-metal contact was prevented

by the oxide film between the two specimens and as a result wear was relatively low.

In certain tests rough, though filmed, areas were observed on specimens which were expected to show smooth, filmed surfaces (see figs. 7 a and b, 8, 9 a and b, and 10 a). It has been pointed out that this might be attributed to the presence of troostite, i.e., the strength of the steels was lower in these spots. It has also been noted that frequently a specimen had a bright, rough, film-free surface during one or more tests and then changed to a filmed surface. This phenomenon may be caused by work-hardening of the surface. Initially these areas may have been too soft to support a film; after a certain amount of wear, however, they work-hardened to such an extent that they were able to support a film. This delayed film formation was noted on many of the specimens in the so-called "border-line group". As the tempering temperature increased this tendency became less marked.

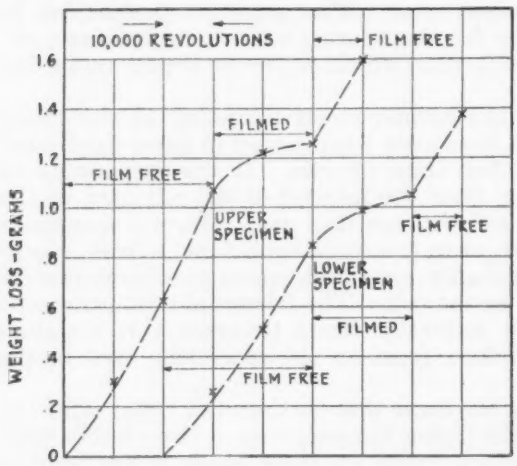

FIGURE 11.—*Weight-loss-revolutions curves showing changes in rates of wear caused by the formation and disappearance of films.*

Steel—0.43 percent carbon, hardened and tempered at 320 C and tested in hydrogen under 60-kg load and 10 percent slip.

It has just been mentioned that this film, once formed, was not removed ordinarily by subsequent wear tests in an oxygen-free atmosphere. Only two exceptions to this statement were noted; these were tests made on specimens of the 0.43 percent carbon steel tempered at 230 C and at 320 C. In both of these cases the type of wear was initially film-free and rough and the rate of wear was high; after several tests of 10,000 revolutions each, films appeared and the wear rate decreased very greatly; after a few further tests the films disappeared and the rate of wear increased at once to its original high value. This behavior is illustrated in detail in figure 11.

The breakdown of the oxide film in these cases may possibly be explained on the basis of excessive deformation of the surface layer, resulting in its disintegration from severe overwork and its subsequent complete removal. A new surface was thus produced which was relatively free of any strengthening effect from cold work. As a consequence the wearing surfaces again became film-free and severe wear took place.

It has been pointed out that the carbon steels tempered below certain temperatures had smooth, filmed, worn surfaces. It is suggested that the presence or absence of severe deformation at the surfaces of the specimens, that is, the relation of the strength and hardness of the steel and the stresses developed during the wearing action, determine the type of wear. On the basis of this hypothesis,

if steels having smooth, filmed surfaces were tested under higher loads, the stresses developed might deform the surface to such an extent as to cause the breakdown of the protective oxide film. This might then result in the transition to film-free surfaces and severe wear. This was tried in the case of the 0.81 percent carbon steel tempered at 260 C, but although the load was raised in steps from 60 to 150 kg, it was impossible to secure film-free surfaces with this steel. The microstructure adjacent to the wearing surface of a specimen of this steel tested under a load of 150 kg showed no more distortion than in the same steel tested under a 60 kg load.

The microscopic study of the structures adjacent to the worn surfaces indicated how wear took place. Deformation of the surface layers of the metal was particularly severe in the case of specimens which had film-free surfaces and severe wear. This severely deformed metal was characterized by numerous lenticular areas which were partially, at times almost completely, outlined by cracks resulting from the severe overwork suffered by the surface metal. These cracks were gradually enlarged and formed paths for the fracture of metallic particles which were then considered to be "worn off" This process is especially well illustrated in figures 5 b, 6 b, 7 b, and 9 b.

Deformation of surface layers of metal was much less noticeable in specimens which had smooth, filmed surfaces and light wear. Severe cold work of the surface frequently took place as evidenced by numerous cracks below the surface. In these specimens, however, the fissures produced by overwork were generally more or less parallel to the wearing surface and did not outline lenticular areas such as were characteristic of the type of wear producing rough, film-free surfaces.

VIII. SUMMARY AND CONCLUSIONS

A study has been made of the influence of oxygen in the atmosphere surrounding specimens of carbon steels subjected to metal-to-metal wear. This work has been undertaken as the initiation of a series of studies of the fundamental factors involved in the wear of metals. These factors have hitherto received too little attention.

An Amsler machine was used to make wear tests on specimens of a hypoeutectoid, a eutectoid and a hypereutectoid carbon steel. Tests were made, both in air and in oxygen-free atmospheres (hydrogen or nitrogen), on specimens which had been given different heat treatments. Microscopic examinations were made of the structures below the wearing surfaces of the specimens after wear tests.

The data obtained indicated:

1. The rates of wear of all the steels when tested in air were low and the worn surfaces were smooth and covered with oxide films.
2. The rates of wear of the steels tempered at low temperatures and tested in an oxygen-free atmosphere were also low and the surfaces were smooth and filmed with oxides. These films, however, were lighter in color and apparently thinner than the films formed during tests in air.
3. The rates of wear of the steels tempered at higher temperatures and tested in an oxygen-free atmosphere were very high and the surfaces were very rough and free from film.

4. Microscopic examinations of the specimens having smooth, filmed, worn surfaces showed that the structures adjacent to these surfaces were somewhat distorted and occasionally contained cracks approximately parallel to the wearing surface. The contours of the worn surfaces appeared smooth even under the microscope.

5. The microstructures adjacent to rough, film-free, worn surfaces were very severely distorted. Numerous cracks, frequently outlining lenticular areas of distorted metal, were characteristic of this type of wear. The contours of these surfaces appeared extremely irregular under the microscope.

6. The results of this study are contradictory to Fink's conclusion that no wear takes place between metallic surfaces if oxygen is absent from the surrounding atmosphere. On the contrary, at least under certain conditions, the absence of oxygen is conducive to greatly increased rates of wear.

WASHINGTON, June 18, 1934.

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